PHILOSOPHICAL

TRANSACTIONS

OF THE

ROYAL SOCIETY

OF

LONDON.

FOR THE YEAR MDCCCL.

PART I.

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THE Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions*, take this opportunity to acquaint the Public, that it fully appears, as well from the Council-books and Journals of the Society, as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication, than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the Public, that their usual meetings were then continued, for the improvement of knowledge, and benefit of mankind, the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed, to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions*; which was accordingly done upon the 26th of March 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings, contained in the several papers so published, which must still rest on the credit or judgement of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body,

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upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

The Meteorological Journal hitherto kept by the Assistant Secretary at the Apartments of the Royal Society, by order of the President and Council, and published in the Philosophical Transactions, has been discontinued. The Government, on the recommendation of the President and Council, has established at the Royal Observatory at Greenwich, under the superintendence of the Astronomer Royal, a Magnetical and Meteorological Observatory, where observations are made on an extended scale, which are regularly published. These, which correspond with the grand scheme of observations now carrying out in different parts of the globe, supersede the necessity of a continuance of the observations made at the Apartments of the Royal Society, which could not be rendered so perfect as was desirable, on account of the imperfections of the locality and the multiplied duties of the observer.

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HER MAJESTY QUEEN VICTORIA, in restoring the Foundation of the Royal Medals, has been graciously pleased to approve the following regulations for the award of them:

That the Royal Medals be given for such papers only as have been presented to the Royal Society, and inserted in their Transactions.

That the triennial Cycle of subjects be the same as that hitherto in operation: viz.

1. Astronomy; Physiology, including the Natural History of Organized Beings.
2. Physics; Geology or Mineralogy.
3. Mathematics; Chemistry.

That, in case no paper, coming within these stipulations, should be considered deserving of the Royal Medal, in any given year, the Council have the power of awarding such Medal to the author of any other paper on either of the several subjects forming the Cycle, that may have been presented to the Society and inserted in their Transactions; preference being given to the subjects of the year immediately preceding: the award being, in such case, subject to the approbation of Her Majesty.

The Council propose to give one of the Royal Medals in the year 1849 for the most important paper in Physics, communicated to the Royal Society after the termination of the Session in June 1845, and prior to the termination of the Session in June 1848, and printed in the Philosophical Transactions.

The Council propose also to give one of the Royal Medals in the year 1849 for the most important paper in Geology or Mineralogy, communicated to the Royal Society after the termination of the Session in June 1845, and prior to the termination of the Session in June 1848, and printed in the Philosophical Transactions.

The Council propose to give one of the Royal Medals in the year 1850 for the most important paper in Mathematics, communicated to the Royal Society after the termination of the Session in June 1846, and prior to the termination of the Session in June 1849, and printed in the Philosophical Transactions.

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The Council propose to give one of the Royal Medals in the year 1851 for the most important paper in Astronomy, communicated to the Royal Society after the termination of the Session in June 1847, and prior to the termination of the Session in June 1850, and printed in the Philosophical Transactions.

The Council propose also to give one of the Royal Medals in the year 1851 for the most important paper in Physiology, including the Natural History of Organized Beings, communicated to the Royal Society after the termination of the Session in June 1847, and prior to the termination of the Session in June 1850, and printed in the Philosophical Transactions.

The Council propose to give one of the Royal Medals in the year 1852 for the most important paper in Physics, communicated to the Royal Society after the termination of the Session in June 1848, and prior to the termination of the Session in June 1851, and printed in the Philosophical Transactions.

The Council propose also to give one of the Royal Medals in the year 1852 for the most important paper in Geology or Mineralogy, communicated to the Royal Society after the termination of the Session in June 1848, and prior to the termination of the Session in June 1851, and printed in the Philosophical Transactions.

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ERRATA.

The plant mentioned by Professor MACAIRE in his paper, published in the Philosophical Transactions for 1848, p. 253, as *Tamus communis*, is not *Smilax aspera*, as suggested in the note at that page, but *Bryonia dioica*.

Page 243, line 9, *for* E *read* F.

—— 257, line 25, *for* light *read* night.

—— 257, line 29, *for* polarity *read* polarization.

PHILOSOPHICAL TRANSACTIONS.

I. The Bakerian Lecture.—*On the Diffusion of Liquids.*

By Thomas Graham, *F.R.S., F.C.S.*

Received November 16,—Read December 20, 1849.

Any saline or other soluble substance, once liquefied and in a state of solution, is evidently spread or diffused uniformly through the mass of the solvent by a spontaneous process.

It has often been asked whether this process is of the nature of the diffusion of gases, but no satisfactory answer to the question appears to be obtained, owing, I believe, to the subject having been studied chiefly in the operations of endosmose, where the action of diffusion is complicated and obscured by the imbibing power of the membrane, which is peculiar for each soluble substance, but no way connected with the diffusibility of the substance in water. Hence also it was not the diffusion of the salt, but rather the diffusion of the solution, which was generally regarded. A diffusibility like that of gases, if it exists in liquids, should afford means for the separation and decomposition even of unequally diffusible substances, and being of a purely physical character, the necessary consequence and index of *density*, should present a scale of densities for substances in the state of solution, analogous to vapour densities, which would be new to molecular theory.

M. Gay-Lussac proceeds upon the assumed analogy of liquid to gaseous diffusion in the remarkable explanation which he suggests of the cold produced on diluting certain saline solutions, namely, that the molecules of the salt expand into the water like a compressed gas admitted into additional space.

The phenomena of solubility are at the same time considered by that acute philosopher as radically different from those of chemical affinity, and as the result of an attraction which is of a physical or mechanical kind. The characters indeed of these two attractions are strongly contrasted. Chemical combination is uniformly attended

with the evolution of heat, while solution is marked with equal constancy by the production of cold. The substances which combine chemically are the dissimilar, while the soluble substance and its solvent are the like or analogous in composition and properties.

In the consideration of solubility, attention is generally engrossed entirely by the quantity of salt dissolved. But it is necessary to apprehend clearly another character of solution, namely, the degree of force with which the salt is held in solution, or the intensity of the solvent attraction, quite irrespective of quantity dissolved. In the two solid crystalline hydrates, pyrophosphate of soda and sulphate of soda, we see the same ten equivalents of water associated with both salts, but obviously united with unequal degrees of force, the one hydrate being persistent in dry air and the other highly efflorescent. So also in the solutions of two salts which are equally soluble in point of quantity, the intensity of the attraction between the salt and the water may be very different, as exemplified in the large but feeble solubility in water of such bodies as the iodide of starch or the sulphindylate of potash, compared with the solubility of hydrochloric acid or of the acetate of potash, which last two substances are capable of precipitating the two former, by displacing them in solution. Witness also the unequal action of animal charcoal in withdrawing different salts from solution, although the salts are equally soluble; and the unequal effect upon the boiling-point of water produced by dissolving in it the same weight of various salts. Besides being said to be small or great, the solubility of a substance has also therefore to be described as weak or strong.

The gradations of intensity observed in the solvent force are particularly referred to, because the inquiry may arise how far these gradations are dependent upon unequal diffusibility; whether indeed rapidity of diffusion is not a measure of the force in question.

I have only further to premise, that two views may be taken of the physical agency by which gaseous diffusion itself is effected, which are equally tenable, being both entirely sufficient to explain the phenomena.

On one theory, that of Dr. Dalton, the diffusibility of a gas is referred immediately to its elasticity. The same spring or self-repulsion of its particles which sends a gas into a vacuum, is supposed to propel it through and among the particles of a different gas.

The existence of an attraction of the particles of one gas for the particles of all other gases is assumed in the other theory. This attraction does not occasion any diminution of volume of gases on mixing, because it is an attraction residing on the surfaces of the gaseous molecules. It is of the same intensity for all gases, hence its effect in bringing about intermixture is dependent upon the weight of the molecules of the gases to be moved by it; and the velocity of diffusion of a gas comes to have the same relation to its density on this hypothesis as upon the other*.

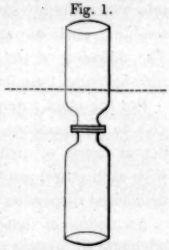
* Both of the molecular theories of the diffusion of gases were first publicly explained, and at the same time ably discussed, with the reference to the law of diffusion which had been drawn from observation, by my late

The surface attraction of molecules assumed will recall the surface attraction of liquids, which is found necessary to account for the elevation of liquids in tubes and other phenomena of capillary attraction.

(1.) An early preliminary experiment was made upon the liquid diffusion of a body, with whose diffusion as a gas we are already well acquainted, namely, carbonic acid dissolved in water.

Two half-pound stoppered glass bottles were selected, of which the mouths were 1·2 inch in diameter, and the lips were ground flat so as to close tight when applied together (fig. 1). One of them, placed firmly in an upright position, was filled to the base of the neck with carbonic acid water. Over this distilled water was poured, care being taken to disturb the liquid below as little as possible, in filling up the neck. The second bottle, filled with distilled water and inverted upon a glass plate, was slipped over the first at the water-trough. The solution of carbonic acid in the lower bottle was thus placed in free communication by an aperture of 1·2 inch, with an equal volume of pure water in the upper bottle. It was expected that the carbonic acid would be found, in time, equally diffused through both bottles.

Fig. 1.



After forty-eight hours, the upper inverted bottle was again slipped off from the lower one, upon a glass plate, and the ratio of the gas found in the upper to that in the lower bottle determined by the weight of carbonate of baryta which the liquids of the two bottles afforded respectively. It was as 1·18 to 12·80 (about 1 to 11), instead of the ratio of equality, which would undoubtedly be the ultimate result of diffusion, were sufficient time allowed.

After five days, in a second experiment with a weaker solution of carbonic acid, the gas was found to be distributed—

In upper bottle	1·63
In lower bottle	8·44

or in the proportion of 1 to 5 nearly.

In other experiments where the liquid in the upper bottle was a solution in water of nitrous oxide gas, instead of pure water, the carbonic acid of the lower bottle was also observed to diffuse into the liquid above it, as freely as it did into pure water in a comparative experiment; the ultimate ratios being 1 to 0·12 in the nitrous oxide liquid, and 1 to 0·10 in the water experiment.

With the necks of the pair of bottles occupied by sponge charged with distilled water, the diffusion of the carbonic acid of the lower bottle proceeded with little

friend Mr. T. S. Thomson of Clitheroe. A decided preference was given by Mr. Thomson, and also by the late Mr. Ivory, to the last, or the attraction theory of diffusion, over that of gases being *vacua* to each other. See Phil. Mag., 3rd series, vol. xxv. pp. 51, 282.

change in its rapidity, or in the result when nitrous oxide was placed above it. The carbonic acid found in the upper bottle, and which had diffused into it from the lower, was 0·231 when the upper bottle contained water alone, and 0·229 when it was water charged with three-fourths of its volume of nitrous oxide gas,—to 1 carbonic acid remaining undiffused in the lower bottle in both cases.

It appeared, then, that the liquid diffusion of carbonic acid was a slow process compared with its gaseous diffusion, quite as much as days are to minutes.

That this diffusion of the liquid carbonic acid takes place with undiminished vigour into water already saturated with nitrous oxide, the substance of all others most resembling carbonic acid in solubility and the whole range of its physical qualities. The diffusion of the liquid carbonic acid appears no more repressed by the liquid nitrous oxide, than the diffusion of gaseous carbonic acid is by gaseous nitrous oxide.

But the chief interest of these observations was the practical solution which they give to the question, whether, in conducting experiments on liquid diffusion, accidental causes of disturbance and intermixture of two liquids, communicating freely with each other, can be avoided. It was made evident that little is to be feared from accidental dispersion when ordinary precautions are taken.

An excess of density in the lower liquid of not more than $\frac{1}{1000}$th part is found adequate to prevent any considerable change of place of the latter,—from expansion by heat, accidental tremors and such disturbing causes, which must exist,—for days together.

(2.) Another early inquiry was, how far is the diffusion of various salts governed or modified by the density of their solutions.

Solutions of eight hydrated acids and salts were prepared, having the common density of 1·200, and were set to diffuse into water in the following manner:—

Eighteen or twenty six-ounce phials were made use of to contain the solutions, and to form what I shall call the Solution phials or cells. They were of the same make and selected from a large stock, of the common aperture of 1·175 inch. Both the mouths and bottoms of these phials were ground flat. The mode of making an experiment was first to fill the phial to the base of the neck, or rather to a constant distance of 0·6 inch below the ground surface of the lip. A little disc of cork, provided with a slight upright peg of wood, was then floated upon the solution in the neck, after having been first dipt in water. The neck itself was now filled up with pure water by means of a pointed sponge, the drop suspended from the sponge being made to touch the peg of the float, and water caused to flow in the gentlest manner, by slightly pressing the sponge. The only other part of the apparatus, the Water-jar, was a plain cylindrical glass jar, of which the inner surface of the bottom was flat or slightly concave, to give a firm support to the phial. The phial, with its solution only, was first placed in this jar partly filled with distilled water, and the neck of the former was then filled up with distilled water in this position, as before described, to avoid any subsequent movement. The phial was ultimately entirely covered to the

depth of an inch with water, which required about 30 ounces of the latter, fig. 2. The saline solution in the diffusion cell or phial thus communicated freely with about 5 times its volume of pure water, the liquid atmosphere which invites diffusion. Another modification of this procedure was the substitution of phials cast in a mould, of the capacity of 4 ounces, or more nearly 2080 grs., which were ground down to a uniform height of 3·8 inches. The neck was 1·25 inch in diameter and 0·5 inch in depth; and the phial was filled up with the solution to be diffused to that point. The solution cell or phial and the water-jar form together a Diffusion cell.

Fig. 2.

The diffusion was stopt, after twenty-seven days in the present experiments, by closing the mouth of the phial with a plate of glass, and then raising it out of the water-jar. The quantity of salt or of acid which had found its way into the water-jar,—the diffusion product as it may be called,—was then determined by evaporating to dryness for the salts, and by neutralizing the same liquid with a normal alkaline solution for the acids. The quantities of the acids diffused are estimated at present as protohydrates for the sake of comparison with the salts.

TABLE I.—Diffusion of Solutions of Density 1·200. Temp. 66° FAHR.

	Placed in solution cell.		Found in water-jar.	
	Proportion of anhydrous salt, or of acid protohydrate, to 100 of water.	Boiling-point.	Diffusion product.	
			In grains.	Ratio.
Chloride of sodium	34·21	225°·5	269·80	100
Nitric acid	37·93	227	581·20	215·42
Sulphuric acid	29·03	223	455·10	168·68
Chloride of potassium (density 1·178)	34·86	221	320·30	118·71
Bisulphate of potash	31·85	216	319·00	118·23
Nitrate of soda	32·42	220	260·20	96·44
Sulphate of magnesia	22·38	214	95·87	35·53
Sulphate of copper	21·56	213½	77·47	28·71

It appears that the diffusion from solutions of the same density is not equal but highly variable, ranging from 1 to 0·1333.

The results also favour the existence of a relation between large or rapid diffusibility and a high boiling-point. The latter property may be taken to indicate of itself a high degree of attraction between the salt and water.

I. CHARACTERS OF LIQUID DIFFUSION.

1. *Diffusion of Chloride of Sodium.*

The characters of liquid diffusion were first examined in detail in the case of this salt.

(1.) Do different proportions of chloride of sodium in solution give corresponding amounts of diffusion?

Solutions were prepared of chloride of sodium in the proportion of 100 water with 1, 2, 3 and 4 parts of the salt.

The diffusion of all the solutions was continued for the same time, eight days, at the mean temperature of 52°·5 Fahr.

Proportion of salt to 100 water.	Diffusion product.	
	In grains.	Ratio.
1	2·78	1·
2	5·54	1·99
3	8·37	3·01
4	11·11	4·00

The quantities diffused appear therefore to be closely in proportion (for this salt) to the quantity of salt in the diffusing solution. The density of the solutions containing 1, 2, 3 and 4 parts of chloride of sodium, was at 60°, 1·0067, 1·0142, 1·0213, 1·0285. The increase of density corresponds very nearly with the proportion of chloride of sodium in solution. A close approach to this direct relation is indeed observable in most salts, when dissolved in proportions not exceeding 4 or 5 per cent.

The relation which appears in these results is also favourable to the accuracy of the method of experimenting pursued. The variation from the speculative result does not in any observation exceed 1 per cent.

(2.) Is the quantity of salt diffused affected by temperature?

The diffusion of similar solutions of chloride of sodium was repeated at two new temperatures, 39°·6 and 67°, the one being above and the other below the preceding temperature. It was necessary to use artificial means to obtain the low temperature owing to the period of the season. A close box of double walls, namely, the ice-safe of the Wenham Ice Company, was employed, masses of ice being laid on the floor of the box, and the water-jars supported on a shelf above. The water and solution were first cooled separately for twenty-four hours in the ice-box, before the diffusion was commenced. It was found that the temperature could be maintained within a range of 2° or 3° for eight days. It was doubtful however whether the temperature was constantly the same to a degree or two in all the jars; and the results obtained at an artificial temperature were always less concordant and sensibly inferior in precision to observations made at the atmospheric temperature.

Diffusion of Chloride of Sodium.

Proportion of salt to 100 water.		Diffusion product.	
		In grains.	Ratio.
1	At 39°·6	2·63	1·
2	At 39°·6	5·27	2·00
3	At 39°·6	7·69	2·92
4	At 39°·6	10·00	3·80
1	At 67°	3·50	1·
2	At 67°	6·89	1·97
3	At 67°	9·90	2·83
4	At 67°	13·60	3·89

The proportionality in the diffusion is still well-preserved at the different temperatures. The deviations are indeed little, if at all, greater than might be occasioned by errors of observation. The ratio of diffusion, for instance, from the solutions containing 4 parts of salt, is 3·80 and 3·89 for the two temperatures, which numbers fall little short of 4.

The diffusion manifestly increases with the temperature, and as far as can be determined by three observations, in direct proportion to the temperature. The diffusion-product from the 4 per cent. solution increases from 10 grs. to 13·60, with a rise of temperature of 27°·4, or rather more than one-third. Supposing the same progression continued, the diffusibility of chloride of sodium would be doubled by a rise of 84 or 85 degrees.

(3.) The progress of the diffusion of chloride of sodium in such experiments as have been narrated, was further studied by intercepting the operation after it had proceeded for different periods of 2, 4, 6 and 8 days. The solution employed was that containing 4 parts of salt to 100 water. Two of the six-ounce phials were diffused at the same time for each period. The temperature given is the mean of the temperatures of a water-jar observed each day of the period. The daily fluctuation was not more than two or three-tenths of a degree Fahr.

In 2 days, temperature 63°·7; the salt diffused was 4·04 and 3·86 grs.; mean 3·95 grs.

In 4 days, temperature 63°·7; the salt diffused was 6·78 and 7·12 grs.; mean 6·95 grs.

In 6 days, temperature 63°·8; the salt diffused was 10·02 and 9·70 grs.; mean 9·86 grs.

In 8 days, temperature 64°; the salt diffused was 13·00 and 13·25 grs.; mean 13·12 grs.

The proportion diffused in the first period of two days is given directly in the first experiments. The proper diffusion for each of the three latter periods of two days is obtained by deducting from the result of each period the result of the period which precedes it:—

Diffused in 1st two days . . . . . 3·95 grs.
Diffused in 2nd two days . . . . . 3·00 grs.
Diffused in 3rd two days . . . . . 2·91 grs.
Diffused in 4th two days . . . . . 3·26 grs.

The diffusion appears to proceed pretty uniformly, if the amount diffused in the first period of two days be excepted. Each of the phials contained at first about 108 grs. of salt, of which the maximum quantity diffused is 13·12 grs. in eight days, or $\frac{1}{8\cdot24}$ of the whole salt. Still the diffusion must necessarily follow a diminishing progression, which would be brought out by continuing the process for longer time, and appear at the earliest period in the salt of most rapid diffusion.

All the experiments which follow being made like the preceding on comparatively large volumes of solution in the phial, and for equally short periods of seven or eight days, may be looked upon as exhibiting pretty accurately the initial diffusion of such solutions, the influence of the diminishing progression being still small. The volume of water in the water-jar is also relatively so large, that the experiment approaches to the condition of diffusion into an Unlimited Atmosphere.

2. *Diffusion of various Salts and other Substances.*

With these notions regarding the influence of temperature and proportion of salt on the amount of diffusion, an examination was next undertaken of the relative diffusibility of a variety of salts and other substances. The results of this first survey I shall state as shortly as possible, as I consider these, as well as the experiments which preceded, as of a preliminary character. The experiments were all made by means of the diffusion phials already described, namely, the six-ounce phials, and with similar manipulations.

In the following experiments, the diffusion took place at a temperature ranging from 62° to 59°, mean 60°·5, and was continued for a period of eight days; the proportion of salt in solution to be diffused being always 20 salt to 100 water, or 1 to 5. I add as usual the density of the solutions.

Table II.—Diffusion of solutions of 20 salt to 100 water, at 60°·5, for eight days.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium	1·1265	58·5	
Chloride of sodium	1·1265	58·87	58·68
Sulphate of magnesia	1·185	27·42	27·42
Nitrate of soda	1·120	52·1	
Nitrate of soda	1·120	51·02	51·56
Sulphate of water	1·108	68·79	
Sulphate of water	1·108	69·86	69·32
Crystallized cane-sugar	1·070	26·74	26·74
Fused cane-sugar	1·066	26·21	26·21
Starch-sugar (glucose)	1·061	26·94	26·94
Treacle of cane-sugar	1·069	32·55	32·55
Gum-arabic	1·060	13·24	13·24
Albumen	1·053	3·08	3·08

The following additional ratios of diffusion were obtained from similar solutions at a somewhat lower temperature, namely 48°;—chloride of sodium 100, hydrate of potash 151·93, ammonia (from a 10 per cent. solution, saturated with chloride of sodium to increase its density) 70, alcohol (saturated with chloride of sodium) 75·74, chloride of calcium 71·23, acetate of lead 45·46.

Where two experiments upon the same salt are recorded in the table they are seen to correspond to within 1 part in 40, which may be considered as the limit of error in the present observations. It will be remarked that the diffusion of cane- and starch-sugar is sensibly equal, and double that of gum-arabic. On the other hand, the sugars have less than half the diffusibility of chloride of sodium. It is remarkable that the specifically lightest and densest solutions, those of the sugars and of sulphate of magnesia, approach each other closely in diffusibility. On comparing together, however, two substances of similar constitution, such as the two salts, chloride of sodium and sulphate of magnesia, that salt appears to be least diffusive of which the solution is densest.

But the most remarkable result is the diffusion of albumen, which is low out of all proportion when compared with saline bodies. The solution employed was the albumen of the egg, without dilution, but strained through calico and deprived of all vesicular matter. As this liquid, with a density of 1·041, contained only 14·69 parts of dry matter to 100 of water, the proportion diffused is increased in the table to that for 20 parts, to correspond with the other substances. In its natural alkaline state the albumen is least diffusive, but when neutralized by acetic acid, a slight precipitation takes place and the liquid filters more easily. The albumen is now sensibly more diffusive than before. Chloride of sodium appears 20 times more diffusible than albumen in the table, but the disparity is really greater; for nearly one-half of the matter which diffused consisted of inorganic salts. Indeed the experiment appears to promise a delicate method of proximate analysis peculiarly adapted for animal fluids. The value of this low diffusibility in retaining the serous or albuminous fluids within the blood-vessels at once suggests itself.

Similar results were obtained with egg albumen diluted and well-beaten with 1 and 2 volumes of water. The solution diluted with an equal bulk of water, and made slightly acid with acetic acid, contained 7½ dry matter to 100 water. Diffused from two four-ounce bottles of 1·25 inch aperture, for seven days, at a mean temperature of 43°·5 Fahr., it gave products of 1·73 and 1·48 gr., from the evaporation of two water-jars, in which cubic crystals of common salt were abundant. The whole matter thus diffused in two cells was found to consist of—

Coagulable albumen	0·94 gr.
Soluble salts	2·27 grs.
	3·21 grs.

The diffusion product of the same solution of albumen left alkaline, or without the

addition of acetic acid, in the same circumstances, was 1·41 and 1·20 grs. in two cells; and consisted of—

Coagulable albumen	0·63 gr.
Soluble salts	1·98 gr.
	2·61 grs.

The diffusion product of a solution of $7\frac{1}{2}$ parts of chloride of sodium to 100 water, from similar cells and for the same time and temperature, would amount to about 30 grs. of salt. It is to be remarked also that 5·53 grs. of the ignited salt diffused from albumen contained 1·32 gr. of potash or 23·9 per cent., which is a high proportion, and indicates that salts of potash diffuse out more freely from albumen than salts of soda.

Nor does albumen impair the diffusion of salts dissolved together with it in the same solution, although the liquid retains its viscosity. Three other substances, added separately in the proportion 5 parts to 100 of the undiluted solution of egg albumen, were found to diffuse out quite as freely from that liquid as they did from an equal volume of pure water: these were chloride of sodium, urea and sugar. Urea proved to be a highly diffusible substance. It nearly coincided in rate with chloride of sodium.

A second series of salts were diffused containing 1 part of salt to 10 of water; a smaller proportion of salt which admits of the comparison of a greater variety of salts. The temperature during the period of eight days was remarkably uniform, 60°—59°.

Table III.—Diffusion of solutions of 10 salt to 100 water at 59°·5.

Name of salt.	Density of solution at 60°.	Anhydrous salt diffused.	
		In grains.	Means.
Chloride of sodium	1·0668	32·3	
Chloride of sodium	1·0668	32·2	32·25
Nitrate of soda	1·0622	30·7	30·7
Chloride of potassium	1·0596	40·15	40·15
Chloride of ammonium	1·0280	40·20	40·20
Nitrate of potash	1·0589	35·1	
Nitrate of potash	1·0589	36·0	35·55
Nitrate of ammonia	1·0382	35·3	35·3
Iodide of potassium	1·0673	37·0	37·0
Chloride of barium	1·0858	27·0	27·0
Sulphate of water	1·0576	37·18	
Sulphate of water	1·0576	36·53	36·85
Sulphate of magnesia	1·0965	15·3	
Sulphate of magnesia	1·0965	15·6	15·45
Sulphate of zinc	1·0984	15·6	
Sulphate of zinc	1·0984	16·0	15·80

Before adverting to the relations in diffusibility which appear to exist between certain salts in the preceding table, I may state the results of the diffusion of the same solutions at a lower temperature.

TABLE IV.—Diffusion of solutions of 10 salt to 100 water at 37°·5.

Name of salt.	Anhydrous salt diffused.	
	In grains.	Means.
Chloride of sodium	22·21	
Chloride of sodium	22·74	22·47
Nitrate of soda	22·53	
Nitrate of soda	23·05	22·79
Chloride of ammonium	31·14	31·14
Nitrate of potash	28·84	
Nitrate of potash	28·56	28·70
Nitrate of ammonia	29·19	29·19
Iodide of potassium	28·10	28·10
Chloride of barium	21·42	21·42
Sulphate of water	31·11	
Sulphate of water	28·60	29·85
Sulphate of magnesia	13·03	
Sulphate of magnesia	13·11	13·07
Sulphate of zinc	11·87	
Sulphate of zinc	13·33	12·60

The near equality of the quantities diffused of certain isomorphous salts is striking at both temperatures. Chloride of potassium and chloride of ammonium give 40·15 and 40·20 grs. respectively in the first table. Nitrate of potash and nitrate of ammonia 35·55 (mean) and 35·3 grs. respectively in the first table, and 28·70 and 29·19 grs. in the second table. Sulphate of magnesia and sulphate of zinc 15·45 and 15·8 grs. (means) in the first table, with 13·07 and 12·60 grs. in the second. The relation observed is the more remarkable, that it is that of equal weights of the salts diffused, and not of atomically equivalent weights. In the salts of ammonia and potash, this equality of diffusion is exhibited also, notwithstanding considerable differences in density between their solutions; the density of the solution of chloride of ammonium, for instance, being 1·0280 and that of chloride of potassium 1·0596. It may have some relation however, but not a simple one, to the density of the solutions; sulphate of magnesia, of which the solution is most dense, being most slowly diffusive; and salts of soda being slower, as they are generally denser in solution, than the corresponding salts of potash. Nor does it depend upon equal solubility, for in none of the pairs is there any approach to equality in that respect.

A comparison was now made of the diffusibility of several acids. They were diffused from the same six-ounce phials, and for eight days. Solutions were prepared in the proportion of 4 parts of the anhydrous acid to 100 parts of water. The quantity of acid which diffused into the water-jar was estimated by the proportion of carbonate of soda which it neutralized.

TABLE V.—Diffusion of acid solutions (4 acid to 100 water) at 59°·3.

Name of acid.	Density of solution at 60°.	Anhydrous acid diffused.	
		In grains.	Means.
Nitric acid	1·0243	29·21	
		28·19	28·7
Hydrochloric acid	1·0225	34·22	
		33·99	34·1
Sulphuric acid	1·0317	18·71	
		18·26	18·48
Acetic acid	1·0094	19·13	
		17·19	18·16
Oxalic acid	1·0235	12·38	
		12·38	12·38
Arsenic acid	1·0320	12·16	
		12·16	12·16
Tartaric acid	1·0194	9·90	
		9·69	9·79
Phosphoric acid	1·0284	9·09	
		9·09	9·09
Chloride of sodium	1·0285	12·32	12·32

Considerable latitude thus appears to exist in the diffusibility of the different acids. To make the result for nitric acid fairly comparable with that for hydrochloric acid, the former should be increased in the proportion of 54 to 63, that is estimated as nitrate of water. This calculation gives 33·5 grs. of nitrate of water diffused, which approaches closely to 34·1 grs., the quantity for chloride of hydrogen or hydrochloric acid. The quantity of soda neutralized by the sulphuric and hydrochloric acids diffused was as 14·32 to 28·97, or nearly as 1 to 2. Sulphuric and acetic acids, on the other hand, appear to be equally diffusible. Phosphoric acid is the least diffusible acid in the series, presenting only about half the diffusion product of the two last-mentioned acids. The solution of phosphoric acid had been boiled for half an hour before diffusion, and was therefore in the tribasic state. The same precaution was not thought of for arsenic acid, although it is possibly required by this acid also. These two acids do not exhibit the equality of diffusion anticipated from their recognized isomorphism, but it is to be stated that the acidimetrical method of analysis followed is not so properly applicable to these two acids as it is to all the others.

3. *Diffusion of Ammoniated Salts of Copper.*

It was interesting to compare together such related salts as sulphate of copper, the ammoniated sulphate of copper or soluble compound of sulphate of copper with 2 equivs. of ammonia and the sulphate of ammonia. It is well known that metallic oxides, or subsalts of metallic oxides, when dissolved in ammonia or the fixed alkalies, are easily taken down by animal charcoal. This does not happen with the ordinary neutral salts of the same acids, which are held in solution by a strong attraction. Supposing the existence of a scale of the solvent attraction of water, the preponderance of the charcoal attraction will mark a term in that scale. And if the solvent

force is nothing more than the diffusive tendency, it will follow that salts which can be taken down by charcoal must be less diffusible than those which cannot.

Of sulphate of ammonia and sulphate of copper, solutions were prepared, consisting of 4 anhydrous salt to 100 water, the sulphate of ammonia being of course taken as $NH_4O.SO_3$. The solution of the copper salt was divided into two portions, one of which had caustic ammonia added to it in slight excess, so as to produce the azure blue solution of ammonio-sulphate of copper.

The solutions were diffused for eight days, at a mean temperature of 64°·9 for the sulphates and nitrates, and 67°·7 for the chlorides.

TABLE VI.—Diffusion of solutions, 4 salt to 100 water.

Name of salt.	Density of solution at temperature of experiment.	Anhydrous salt diffused in grains.
Sulphate of ammonia	1·0235	12·13
Sulphate of ammonia	1·0235	11·96
Sulphate of copper	1·0369	6·19
Sulphate of copper	1·0369	6·51
Ammonio-sulphate of copper	1·0308	1·45
Ammonio-sulphate of copper	1·0308	1·43
Nitrate of ammonia	1·0136	16·15
Nitrate of ammonia	1·0136	15·44
Nitrate of copper	1·0323	9·77
Nitrate of copper	1·0323	9·77
Ammonio-nitrate of copper	1·0228	1·77
Ammonio-nitrate of copper	1·0228	1·36
Chloride of ammonium	1·0100	16·18
Chloride of ammonium	1·0100	17·00
Chloride of copper	1·0328	10·83
Chloride of copper	1·0328	10·48
Ammonio-chloride of copper	1·0209	4·54
Ammonio-chloride of copper	1·0209	3·94

It is to be observed, that in preparing the ammoniated salts, the solutions of the neutral salts of copper were slightly diluted by the water of the solution of ammonia added to them, so that the proportion of salt of copper which they possessed was sensibly reduced below 4 per cent. On the other hand, the copper salt which diffused out is estimated, not as ammoniated, but as neutral salt. It will be observed that the quantity of sulphate of copper diffused out in the experiments falls from 6·35 in the neutral salt to 1·44 gr. in the ammoniated salt; of nitrate of copper from 9·77 to 1·56, and of chloride of copper from 10·65 to 4·24. These numbers are to be taken only as approximations; they are sufficient however to prove a much reduced diffusibility in the ammoniated salts of copper.

It will be remarked that the nitrate of ammonia and chloride of ammonium approximate, 15·80 and 16·59 grs.; as do also the nitrate and chloride of copper, 9·77 and 10·65 grs.; the chlorides, which were diffused at the higher temperature by 2°·8, exceeding the nitrates in both cases.

4. *Diffusion of Mixed Salts.*

When two salts can be mixed without combining, it is to be expected that they will diffuse separately and independently of each other, each salt following its special rate of diffusion.

(1.) Anhydrous sulphate of magnesia and sulphate of water (oil of vitriol), one part of each, were dissolved together in 10 parts of water, and the solution allowed to diffuse for four days at 61°·5.

The water-jar was found to have acquired—

Sulphate of magnesia . . .	5·60 grs.
Sulphate of water	21·92 grs.
	27·52 grs.

The experiment with the same diffusion cell and liquid being continued for a second period, this time of eight days, there was found to be simultaneously diffused, of—

Sulphate of magnesia . . .	9·46 grs.
Sulphate of water	29·32 grs.
	38·78 grs.

It is obvious that the inequality should be greatest in the first period of diffusion, or with the initial diffusion, as it actually appears above, and become less and less sensible as the proportion of the low diffusive salt comes to be increased in the solution phial.

In former experiments upon the solution of sulphate of magnesia alone in water, as 1 salt to 10 water, compared with sulphate of water, also as 1 to 10, the disparity in the diffusion of these two salts was less considerable, being only as 1 to 2·385, instead of 1 to 3 or 4.

(2.) A solution was also diffused of 1 part of anhydrous sulphate of soda and 1 part of chloride of sodium in 10 parts of water, for four days at 61°·5. The salt which diffused out in that time consisted of—

Sulphate of soda	9·48 grs.
Chloride of sodium	17·80 grs.
	27·28 grs.

The sulphate of soda in the last experiment had begun to crystallize in the solution phial, from a slight fall of temperature, before the diffusion was interrupted, a circumstance which may have contributed to increase the inequality of the proportions diffused of these two salts.

(3.) A solution of equal weights of anhydrous carbonate of soda and chloride of sodium, namely, of 4 parts of the one salt and 4 parts of the other, to 100 water, was diffused from 3 four-ounce phials of 1·25 inch aperture, at a mean temperature of 57°·9 and for seven days. The diffusion product amounted to 17·10, 17·58 and 18·13 grs.

of mixed salt in the three experiments. The analysis of the last product of 18·13 grs. gave—

Carbonate of soda	5·68	31·33
Chloride of sodium	12·45	68·67
	18·13	100·00

Here the carbonate of soda presents a diffusion less than one-half of that of chloride of sodium. The difference is again greater than the peculiar diffusibilities of the same salts as they appear when the salts are separately diffused. For in experiments made in the same phials with solutions of 4 parts of each salt singly to 100 water, but with a lower temperature by 3°·6, namely, at 54°·3, the diffusion product of the carbonate of soda was 7·17 and 7·34 grs. in two experiments, of which the mean is 7·25 grs.; while the diffusion product of the chloride of sodium was 11·18 and 10·73 grs. in two experiments, of which the mean is 10·95 grs. The quantity of chloride of sodium diffused being taken at 100 in both sets of experiments, we have diffused—

Of carbonate of soda 66·18, when diffused singly.

Of carbonate of soda 45·64, when diffused with chloride of sodium.

The least soluble of the two salts appears in all cases to have its diffusibility lessened in the mixed state. The tendency to crystallization of the least soluble salt must evidently be increased by the admixture. Now it is this tendency, or perhaps more generally the increased attraction of the particles of a salt for each other, when approximated by concentration, which most resists the diffusion of a salt, and appears to weaken the diffusive force in mixtures, as it is also found to do so in a strong solution of a single salt.

(4.) Equal weights of nitrates of potash and ammonia dissolved, as in certain preceding experiments, in five times the weight of the mixed salts of water, and diffused for eight days, gave in two experiments—

	At 59°·4.	At 52°·6.
Nitrate of potash	28·39	25·88
Nitrate of ammonia	36·16	30·36
	64·55	56·24

The inequality in the diffusion of these two nitrates is singular, considering that in solutions of 1 salt to 10 water, they appeared before to be equally diffusive. But on now comparing the diffusion of solutions of 1 salt to 5 water, at 52°·6, the salts no longer diffused in equal proportions:—

Nitrate of potash gave . . . . 57·93 grs.

Nitrate of ammonia gave . . . . 82·08 grs.

The solution of nitrate of potash last diffused was nearly a saturated one, while that of nitrate of ammonia is far from being so. The first has its diffusibility, in consequence, impaired, and falls considerably below the second.

The relatively diminished diffusibility of sulphate of magnesia, when associated with sulphate of water, is probably connected with a similar circumstance; sulphate of magnesia being less soluble in dilute sulphuric acid than in pure water.

(5.) The salt which diffused from a strong solution of sulphates of zinc and magnesia, consisting of 1 part of each of these salts in the anhydrous state and 6 parts of water, did not consist of the two salts in exactly equal proportions. The mixture of salts, diffused for eight days, as in the late experiments, gave the following results:—

	Exp. I.	II.	III.
Sulphate of zinc	8·12	7·49	8·12
Sulphate of magnesia	8·68	8·60	8·75
	16·80	16·09	16·87

There is therefore always a slight but decided preponderance of sulphate of magnesia, the more soluble salt, in the diffusion product. These last experiments were made at an early period with another object in view, namely, to ascertain whether in closely related salts, such as the present sulphates of magnesia and zinc, the two salts might be elastic to each other, like the particles of one and the same salt, so that one salt might possibly suppress the diffusion of the other, and diffuse alone for both. The experiments lend no support to such an idea.

It appears from all the preceding experiments, that the inequality of diffusion which existed, is not diminished but exaggerated in mixtures, a curious circumstance, which has also been observed of mixed gases.

5. *Separation of Salts of different Bases by Diffusion.*

It was now evident that inequality of diffusion supplies a method for the separation, to a certain extent, of some salts from each other, analogous in principle to the separation of unequally volatile substances by the process of distillation. The potash salts appearing to be always more diffusive than the corresponding soda salts, it follows, that if a mixed solution of two such salts be placed in the solution phial, the potash salt should escape into the water atmosphere in largest proportion, and the soda salt be relatively concentrated in the phial. This anticipation was fully verified.

(1.) A solution was prepared of equal parts of the anhydrous carbonates of potash and soda in 5 times the weight of the mixture of water. Diffused from a small thousand-grain phial of 1·1 inch aperture, into 6 ounces of water, for nineteen days, at a temperature above 60°, it gave a liquid of density 1·0350, containing a considerable quantity of the salts. Of these mixed salts, converted into chlorides by the addition of hydrochloric acid, 9·39 grs., being treated with bichloride of platinum in the usual manner, gave 19·39 grs. of the double chloride of platinum and potassium, equivalent to 5·91 grs. of chloride of potassium; and left in solution 3·44 grs. of chloride of sodium: loss 0·04 gr. These chlorides represent 5·46 grs. of carbonate of potash and

3·12 grs. of carbonate of soda. The salts actually diffused out were therefore in the proportion of—

Carbonate of soda	36·37
Carbonate of potash	63·63
	100·00

(2.) In another similar experiment from a six-ounce phial into 8½ ounces of water, the liquid of the water-jar, after twenty-five days' diffusion, contained the two carbonates in nearly the same proportions as before, namely—

Carbonate of soda	35·2
Carbonate of potash	64·8
	100·0

(3.) A partial separation of the salts of sea-water was effected in a similar manner. The sea-water (from Brighton) was of density 1·0265. One thousand grs. of the liquid yielded 35·50 grs. of dry salts, of which 2·165 grs. were magnesia. The dry salts contain therefore 6·10 per cent. of that earth.

Six thousand-grain phials, of 1·1 inch aperture, were properly filled with the sea-water and placed in six tumblers, each of the last containing 6 ounces of water. Temperature about 50°. The diffusion was interrupted after eight days. The salts of the sea-water were now found to be divided as follows:—

Diffused into the tumblers	92·9 grs., or	36·57 per cent.
Remaining in the phials	161·1 grs., or	63·43 per cent.
	254·0	100·00

Rather more than one-third of the salts has therefore been transferred from the solution phials to the water-jars by diffusion.

Of the diffused salts in the tumblers, 46·5 grs. were found to contain 1·90 gr. magnesia, or 4·09 per cent. Hence we have the following result:—

Magnesia originally in salts of sea-water . . .	6·01 per cent.
Magnesia in salts diffused from sea-water . . .	4·09 per cent.

The magnesia, also, must in consequence be relatively concentrated in the liquid remaining behind in the diffusion cells.

A probable explanation may be drawn from the last results of the remarkable discordance in the analysis of the waters of the Dead Sea, made by different chemists of eminence. I refer to the relative proportion of the salts, and not their absolute quantity, the last necessarily varying with the state of dilution of the saline water when taken up. The lake in question falls in level 10 or 12 feet every year, by evaporation. A sheet of fresh water of that depth is thrown over the lake in the wet season, which water may be supposed to flow over a fluid nearly 1·2 in density, without greatly disturbing it. The salts rise from below into the superior stratum

by the diffusive process, which will bring up salts of the alkalies with more rapidity than salts of the earth, and chlorides, of either class, more rapidly than sulphates. The composition of water near the surface must therefore vary greatly, as this process is more or less advanced.

(4.) I may be allowed to add another experiment which is curious for the protracted immobility of a column of water which it exhibits, as well as for the separation occurring, which last may be interesting also in a geological point of view. A plain glass cylinder with a foot, 11 inches in height, and of which the capacity was 64 cubic inches, had 8 cubic inches poured into it of a saturated solution of carbonate of lime in carbonic acid water, containing also 200 grs. of chloride of sodium dissolved. Distilled water was then carefully poured over the saline solution, so as to fill up the jar, a float being used and the liquid disturbed as little as possible in the operation. The mouth of the jar was lastly closed by a ground glass plate, and it was left undisturbed upon the mantelpiece of a room without a fire, from March 20 to September 24 of the present year, or for six months and four days. Afterwards, on removing the cover, the fluid was observed not to have evaporated sensibly, and it exhibited no visible deposit. This I was not surprised at, as no deposit appeared in a similar experiment with the jar uncovered, after the lapse of six weeks. The liquid in the former jar was now carefully drawn off by a small siphon with the extremity of both its limbs recurved so as to open upwards, in four equal portions, which may be numbered from above downwards. Equal quantities of the four strata of liquids gave the following proportions of chloride of sodium and carbonate of lime:—

	Chloride of sodium.	Carbonate of lime.
No. 1.	21·91	0·10
No. 2.	23·41	0·22
No. 3.	23·55	0·38
No. 4.	23·99	0·42

The diffusion of the chloride of sodium has therefore not yet reached complete uniformity, although approaching it, the proportion of that salt obtained from the top and bottom strata being as 11 to 12. But the diffusion of the carbonate of lime appears much less advanced, the proportion of that substance being as 1 to 4 at the top and bottom of the liquid column. The slight difference in density of the strata, it may be further remarked, must have been sufficient to preserve such a column of liquid entirely quiescent, as shown by the distribution of the carbonate of lime, during the considerable changes of temperature of the season.

Chemical analysis, which gives with accuracy the proportions of acids and bases in a solution, furnishes no means of deciding how these acids and bases are combined, or what salts exist in solution. But it is possible that light may be thrown on the constitution of mixed salts, at least when they are of unequal diffusibility, by means of a diffusion experiment. With reference to sea-water, for instance, it has been a question in what form the magnesia exists, as chloride or as sulphate; or how much

exists in the one form and how much in the other. Knowing however the different rates of diffusibility of these two salts, which is nearly chloride 2 and sulphate 1, and their relation to the diffusibility of chloride of sodium, we should be able to judge from the proportion in which the magnesia travels in company with chloride of sodium, whether it is travelling in the large proportion of chloride of magnesium, in the small proportion of sulphate of magnesia, or in the intermediate proportion of a certain mixture of chloride and sulphate of magnesia. But here we are met by a difficulty. Do the chloride of magnesium and sulphate of magnesia necessarily pre-exist in sea-water in the proportions in which they are found to diffuse? May not the more easy diffusion of chlorides determine their formation in the diffusive act, just as evaporation determines the formation of a volatile salt—producing carbonate of ammonia, for instance, from hydrochlorate of ammonia with carbonate of lime in the same solution? We shall see immediately that liquid diffusion, as well as gaseous evaporation, can produce chemical decompositions.

6. *Decomposition of Salts by Diffusion.*

(1.) At an early period of the inquiry, a solution was diffused of bisulphate of potash, saturated at 68° and of density 1·280, from the six-ounce phial of 1·175 inch aperture, into 20 ounces of water. The period of diffusion extended to fifty days. About the middle of that period, a few small crystals of sulphate of potash, amounting probably to 3 or 4 hundredths of a grain, appeared in the diffusion cell and never afterwards dissolved away. When terminated, the liquid remaining in the solution cell was found of density 1·154; that in the water-jar 1·0326. A portion of the latter liquid gave by analysis—

Sulphate of potash	20·37	} Bisulphate of potash.
Sulphate of water	11·47	
Sulphate of water	12·77	
	44·61	

It thus appears that the bisulphate of potash undergoes decomposition in diffusing, and that the acid diffuses away to about double the extent, in equivalents, of the sulphate of potash. This greater escape of the acid will also account for the deposition of crystals of the neutral sulphate in the solution cell.

(2.) A similar experiment was made with another double sulphate of greater stability, common potash-alum. The solution of 4 anhydrous alum in 100 water, was diffused from the six-ounce phial into 24 ounces of water, at 64°·2, for eight days. The quantity of salt diffused in that time amounted only to 7·48 grs. It contained 1·06 gr. alumina, which is equivalent to 5·33 grs. of alum. The diffused salt gave off no acid vapours at 600°. We may therefore suppose the excess of salt which is diffused to be sulphate of potash. The diffusion product of alum, at 64°, appears to be—

Alum	5·33	71·26
Sulphate of potash . . .	2·15	28·74
	7·48	100·00

In a second experiment, the diffusion product amounted to 6·39 grs., of which 0·95 gr. was alumina; and it is represented by 4·77 alum and 1·52 sulphate of potash.

In connexion with the low diffusibility of the sulphate of alumina of alum, it was found that the addition of caustic potash to the alum solution, so as to convert it into an aluminate of potash, increased the diffusibility of the alumina. The diffusion product from the 4 per cent. solution of alum so treated contained 1·62 gr. of alumina in one experiment and 1·54 in another.

As alum is a salt of great stability, it presents a severe test of the influence in question. The decomposition of this double salt by diffusion was further confirmed therefore in experiments made by means of the four-ounce diffusion phials of 1·25 inch aperture, and the alteration which the salt undergoes in the process more exactly ascertained. The experiments were made at a mean temperature of 57°·9, and lasted seven days; the solution employed being of 4 anhydrous alum to 100 water, as before.

In three experiments, the salt diffused out amounted to 5·73, 5·80 and 5·65 grs.; of which the mean is 5·73 grs. The latter quantity gave 0·82 alumina and 3·22 sulphuric acid, which correspond to 4·11 anhydrous alum and 1·62 neutral sulphate of potash. Or, we have as the diffusion product of alum, in 100 parts—

Alum	71·73
Sulphate of potash	28·27
	100·00

This analysis corresponds closely with the diffusion product of the former experiments, which gave 71·26 per cent. of alum. The solution of alum which remains behind in the solution phials must of course acquire an excess of sulphate of alumina.

The salt, sulphate of alumina, did not appear to be decomposed when diffused alone. A four per cent. solution of the hydrated sulphate of alumina, which is manufactured at Newcastle, when diffused in the same circumstances as the preceding solutions of alum, gave 3·40 grs. of anhydrous sulphate of alumina, in which the acid was to the alumina as 2·95 equivalents of the former to 1 equivalent of the latter, or as nearly as possible in the proportion of 3 equivalents of acid to 1 of base. As the Newcastle salt contained almost exactly half its weight of water, the 3·40 grs. of anhydrous salt diffused out are equivalent to 6·80 grs. of hydrated sulphate of alumina. The sulphate of alumina appears thus to be more diffusive than the double sulphate of alumina and potash, in the proportion of 6·80 to 5·73.

(3.) It was interesting to observe what really diffuses from the ammoniated sulphate of copper ($CuO, SO_3, 2NH_3+HO$), and to find if the low diffusibility of that salt is attended with decomposition. The diffusion of the ammoniated sulphate of copper was therefore repeated from a 4 per cent. solution in the six-ounce solution phial, for eight days, at 64°·2. In evaporating the water of the jar afterwards, the ammoniated sulphate of copper present was necessarily decomposed, by the escape of ammonia, and a subsulphate of copper precipitated. The copper found, however, was

estimated as neutral sulphate of copper. The diffusion product of two experiments may be represented as follows, in grains:—

	I.	II.
Sulphate of copper	0·81	0·97
Sulphate of ammonia	5·46	5·53
	6·27	6·50

The abundant formation and separation of sulphate of ammonia in these experiments, prove that the ammoniated sulphate of copper is largely decomposed in diffusion.

(4.) Perhaps the most interesting result of this kind is a solution which is given of the problem of the decomposition of the alkaline sulphates by means of lime.

Solutions were prepared of ½ per cent. of sulphate of potash and of chlorides of potassium and sodium in lime-water. Two solution phials were filled with each of these solutions, and placed for diffusion in water-jars filled with lime-water, at 49°, for seven days.

In the sulphate no deposition of crystallized sulphate of lime took place within the solution phial, while the water-jar acquired an alkaline reaction, which remained after precipitating the lime entirely by carbonic acid gas and evaporating twice to dryness. Hydrate of potash, it will afterwards appear, is an eminently diffusive salt, having double the diffusibility of sulphate of potash. The tendency of the former to diffuse enables the affinity of the lime for sulphuric acid to prevail, and the alkali is liberated and diffused away into the external atmosphere of lime-water. By the latter, hydrate of lime is returned to the solution cell and the decomposition continued. The salt diffused in the two cells amounted to 2·60 grs., of which 0·62 gr., or 23·85 per cent., was hydrate of potash. The chlorides of potassium and sodium, on the contrary, were not sensibly decomposed.

It is known that a precipitation of sulphate of lime may occur, with a larger proportion of sulphate of potash in lime-water, in a close phial without external diffusion. As the decomposition of the sulphate of potash, in the latter case, has been referred to the insolubility of the sulphate of lime, so the decomposition in the former circumstances is referred, in a similar sense, to the high diffusibility of hydrate of potash.

7. *Diffusion of Double Salts.*

How is the diffusion of two salts affected by their condition of combination as a double salt? A solution of the double sulphate of magnesia and potash, in the proportion of 100 water to 4 anhydrous salt, was operated upon in the four-ounce diffusion phials of 1·25 inch aperture, with a period of diffusion of seven days, at 57°·9 Fahr. The diffusion product of the double salt was 8·09 and 7·81 grs. in two experiments: mean, 7·95 grs.

The constituent salts, sulphate of magnesia and sulphate of potash, were now dis-

solved separately, in the proportions in which they existed in the double salt, namely, 1·65 gr. anhydrous sulphate of magnesia in 100 water, and 2·35 grs. sulphate of potash in 100 water, making up together 4 parts of salts. The two solutions thus contain equivalent quantities of the different sulphates.

The separate diffusion of the sulphate of magnesia was 2·09, 2·11 and 2·40 grs. in three cells; and of the sulphate of potash, 5·83, 5·97 and 5·54 grs. in three cells; the circumstances of the experiments being the same as those of the double salt. The means of the two salts are 2·20 and 5·78 grs.; and the sum of the two means 7·98 grs. The result is, that the separate diffusion of the constituent salts is almost identical with their diffusion when combined as a double salt:—

Diffusion of the double sulphate of magnesia and potash . . .	7·95 grs.
Diffusion of equivalents of sulphate of magnesia and sulphate of potash in separate cells	7·98 grs.

It would thus appear that the diffusibility of this double salt is the sum of the separate diffusions of its constituent salts.

It has been a question whether a double salt is formed at once when its constituent salts are dissolved together, or not till the act of crystallization of the compound salt. Equivalents of the same two sulphates, making up 4 parts, were dissolved together without heat in 100 water. Now the diffusion from this mixture, which has the composition of the preceding solution of the double salt, exhibited notwithstanding a sensibly different result of diffusion, giving 7·28, 7·37 and 7·26 grs. in three cells mean, 7·30 grs. The diffusion of the double salt was greater, namely, 7·95 grs. Hence a strong presumption that the mixed salts last diffused were not combined, and that the double sulphate of magnesia and potash is not necessarily formed immediately upon dissolving together its constituent salts.

In early experiments of a similar nature made upon the double salt, sulphate of copper and potash, and upon a mixture of the two sulphates newly dissolved together, a similar result was obtained. While the diffusion of the mixed salts was 25·6 grs., that of the same weight of the combined salts (the double sulphate) was 30 grs. The double salt appears more diffusible, in both cases, than its mixed constituents.

These double salts appear to dissolve in water without decomposition, although the single salts may meet in solution without combining. Hence in a mixture of salts we may have more than one state of equilibrium possible. And when a salt, like alum, happens to be dissolved in such a way as to decompose it, the constituents are not necessarily reunited by subsequent mixing. Many practices in the chemical arts, which seem empirical, have their foundation possibly in facts of this kind.

8. *Diffusion of one Salt into the Solution of another Salt.*

It was curious and peculiarly important, in reference to the relation of liquid to gaseous diffusion, to find whether one salt A would diffuse into water already charged

with an equal or greater quantity of another salt B, as a gas *a* freely diffuses into the space already occupied by another gas *b*; the gas *b* in return diffusing at the same time into the space occupied by *a*. Or whether, on the contrary, the diffusion of the salt A is resisted by B. The latter result would indicate a neutralization of the water's attraction, and a kind of equivalency or equality of power and exchangeability of different salts, in respect of that effect, which would divide entirely the phenomena of liquid from those of gaseous diffusion.

(1.) A solution of 4 parts of carbonate of soda to 100 water, of density 1·0406, was placed in the six-ounce diffusion phial of 1·175 inch aperture, and allowed to communicate with 24 ounces of water.

Two similar diffusion phials, equally charged, were immersed in 24 ounces of a solution of 4 parts of chloride of sodium to 100 water, having the density 1·0282. The diffusion proceeded for eight days, in all cases, at 64°. The proportion of carbonate of soda found without in the water-jar afterwards, was ascertained by an alkalimetrical process, the neutralization being effected at the boiling-point. The following are the results:—

Experiment I. Diffusion product into water . . . 9·06 grs. of carbonate of soda.

Experiment II. Diffusion product into solution of chloride of sodium . . . . . } 8·82 grs. of carbonate of soda.

Experiment III. Diffusion product into solution of chloride of sodium . . . . . } 9·10 grs. of carbonate of soda.

It thus appears that 4 per cent. of chloride of sodium present in the water atmosphere of the jar has no sensible effect in retarding the diffusion into it, from the solution cell, of carbonate of soda from a solution containing also 4 per cent. of the latter.

(2.) The experiment was varied by allowing the solution of carbonate of soda to diffuse into a solution of sulphate of soda, a salt more similar to the former in solubility and composition. The solution of the latter, containing 4 per cent., was of density 1·0352. The temperature and period of diffusion were the same as before:—

Experiment IV. Diffusion product into solution of sulphate of soda . . . . . } 7·84 grs. of carbonate of soda.

Experiment V. Diffusion product into solution of sulphate of soda . . . . . } 7·82 grs. of carbonate of soda.

Here we find a small reduction in the quantity of carbonate of soda diffused, amounting to one-eighth of the whole. The sulphate of soda has therefore exercised a positive interference in checking the diffusion of the carbonate to that extent. So small and disproportionate an effect however is scarcely sufficient to establish the existence of a mutual elasticity and resistance between these two salts.

Still it might be said, may not the diffusion of one salt be resisted by another salt which is strictly isomorphous with the first?

(3.) A solution of 4 parts of nitrate of potash to 100 of water, of density 1·0241, placed in the solution phial, was allowed to communicate with water containing 4 per cent. of nitrate of ammonia in the water-jar, which last solution was of density 1·0136; with all other circumstances as before. With one solution phial having the usual aperture, 1·175 inch, the diffusion product was 15·32 grs. of nitrate of potash. With a second phial, having a larger aperture of 1·190 inch, the diffusion product was 18·03 grs. of nitrate of potash. No comparative experiment, on the diffusion of nitrate of potash into water, was made at the same time. But nitrate of ammonia, which appeared before to coincide in diffusibility with nitrate of potash, gave on a former occasion, in similar circumstances, and at 64°·9, nearly the same temperature, a diffusion product of 15·80 grs. The quantity of nitrate of potash (15·32 grs.) which diffused into the solution of nitrate of ammonia approaches so closely to the number quoted, that we may safely conclude that the diffusion of nitrate of potash is not sensibly resisted by nitrate of ammonia, although these two salts are closely isomorphous. They are still therefore inelastic to each other, like two different gases.

These experiments have been made upon dilute solutions, and it is not at all impossible that the result may be greatly modified in concentrated solutions of the same salts, or when the solutions approach to saturation. But there is reason to apprehend that the phenomena of liquid diffusion are exhibited in the simplest form by dilute solutions, and that concentration of the dissolved salt, like compression of a gas, is attended often with a departure from the normal character.

On approaching the degree of pressure which occasions the liquefaction of a gas, an attraction appears to be brought into play, which impairs the elasticity of the gas; so on approaching the point of saturation of a salt, an attraction of the salt molecules for each other, tending to produce crystallization, comes into action, which will interfere with and diminish that elasticity or dispersive tendency of the dissolved salt which occasions its diffusion.

We are perhaps justified in extending the analogy a step further between the characters of a gas near its point of liquefaction and the conditions which we may assign to solutions. The theoretical density of a liquefiable gas may be completely disguised under great pressure. Thus, under a reduction by pressure of 20 volumes into 1, while the elasticity of air is 19·72 atmospheres, that of carbonic acid is only 16·70 atmospheres, and the deviation from their normal densities is in the inverse proportion. Of salts in solution the densities may be affected by similar causes, so that although different salts in solution really admit of certain normal relations in density, these relations may be concealed and not directly observable.

The analogy of liquid diffusion to gaseous diffusion and vaporization is borne out in every character of the former which has been examined. Mixed salts appear to diffuse independently of each other, like mixed gases, and into a water atmosphere already charged with another salt as into pure water. Salts also are unequally diffusible, like the gases, and separations, both mechanical and chemical (decompositions), are

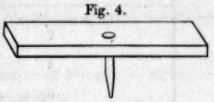
produced by liquid as well as by gaseous diffusion. But it still remains to be found whether the diffusibilities of different salts are in any fixed proportion to each other, as simple numerical relations are known to prevail in the diffusion velocities of the gases, from which their densities are deducible.

It was desirable to make numerous simultaneous observations on the salts compared, in order to secure uniformity of conditions, particularly of temperature. The means of greatly multiplying the experiments were obtained by having the solution phial cast in a mould, so that any number of solution cells could be procured of the same form and dimensions. The phials were of the form represented (fig. 3), holding about 4 ounces, or more nearly 2080 grs. of water to the base of the neck, and the mouths of all were ground down, so as to give the phial a uniform height of 3·8 inches. The mouth or neck was also ground to fit a gauge-stopper of wood, which was 0·5 inch deep and slightly conical, being 1·24 inch in diameter on the upper, and 1·20 inch on the lower surface. These are therefore the dimensions of the diffusion aperture of the new solution cells.

Fig. 3.

A little contrivance to be used in filling the phials to a constant distance of half an inch from the surface of the lip, proved useful. It was a narrow slip of brass plate, having a descending pin of exactly half an inch in length fixed on one side of it (fig. 4). This being laid across the mouth of the phial with the pin downwards in the neck, the solution was poured into the phial till it reached the point of the pin. The brass plate and pin being removed, the neck was then filled up with distilled water, with the aid of the little float as before described. The water-jar, in which the solution phial stood, was filled up with water also as formerly, so as to cover the phial entirely to the depth of 1 inch. This water atmosphere amounted to 8750 grs., or about 20 ounces. A glass plate was placed upon the mouth of the water-jar itself to prevent evaporation. Sometimes 80 or 100 diffusion cells were put in action at the same time. The period of diffusion chosen was now always exactly seven days, unless otherwise mentioned.

Fig. 4.



II. DIFFUSION OF SALTS OF POTASH AND AMMONIA.

Solutions were prepared of the various salts, in a pure state, in certain fixed proportions, namely, 2, 4, 6$\frac{2}{3}$ and 10 parts of salt to 100 parts of water by weight. The density of these solutions was observed by the weighing-bottle, at 60°. The solutions were frequently diffused at two different temperatures; one, the temperature of the atmosphere, which was fortunately remarkably constant during most of the experiments to be recorded at present, and the other, a lower temperature, obtained in a close box of large dimensions, containing masses of ice. The results at the artificial temperature were obviously less accurate than those of the natural temperature, but have still considerable value. Three experiments were generally made upon the diffusion of each solution at the higher, with two experiments at the lower temperature.

(1.) The carbonate and sulphate of potash and sulphate of ammonia were first diffused during a period of seven days, of which the temperatures observed by a thermometer placed near the water-jars were 64°·5, 65°, 63°·5, 63°, 63°, 63°·5, 65° and 66°; mean temperature 64°·2.

TABLE VII.—Diffusion of Carbonate of Potash, Sulphate of Potash and Sulphate of Ammonia.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°·2.		At 37°·6.	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of potash.					
2	1·0178	5·36		3·80	
		5·55	5·45	3·91	3·85
4	1·0347	10·39		6·99	
		10·11	10·25	7·19	7·09
$6\frac{2}{3}$	1·0572	16·50		11·42	
		16·46		11·08	11·25
		17·05	16·67		
10	1·0824	24·42			
		24·94			
		24·70	24·69		
Sulphate of potash.					
2	1·0155	5·62		3·93	
		5·42	5·52	3·98	3·95
4	1·0318	10·49		7·50	
		10·65	10·57	7·31	7·40
$6\frac{2}{3}$	1·0512	17·07		11·62	
		16·89		11·71	11·66
		17·54	17·17		
10	1·0742	23·40			
		23·59			
		23·88	23·62		
Sulphate of ammonia, $NH_4O.SO_3$.					
2	1·0117	5·71		3·73	
		5·45	5·58	3·79	3·76
4	1·0229	10·72		7·54	
		10·30	10·51	7·86	7·70
$6\frac{2}{3}$	1·0369	17·28		10·94	
		16·28		10·98	10·96
		16·80	16·79		
10	1·0529	21·86			
		22·49			
		22·25	22·20		

The diffusion product was obtained by evaporating the water of each jar separately as before, and the result is expressed in grains.

It will be observed at once, on comparing the means of the experiments, that the three salts under consideration are remarkably similar in their diffusion, particularly with the smaller proportions of salt. Thus the mean diffusion of the 2, 4, $6\frac{2}{3}$ and 10 parts of the salts is as follows:—

Diffusion at 64°·2.

	2.	4.	6⅔.	10.
Carbonate of potash	5·45	10·25	16·67	24·69
Sulphate of potash	5·52	10·57	17·17	23·62
Sulphate of ammonia	5·58	10·51	16·79	22·20

Diffusion at 37°·6.

	2.	4.	6⅔.
Carbonate of potash	3·85	7·09	11·25
Sulphate of potash	3·95	7·40	11·66
Sulphate of ammonia	3·76	7·70	10·96

The proportions diffused are sensibly equal, of the different salts, at the higher temperature, with the exception of the largest proportion of salt, 10 per cent., when a certain divergence occurs. This last fact is consistent with our expectations, that the diffusion of salts would prove most highly normal in dilute solutions. Some of the irregularities at the lower temperature are evidently of an accidental kind.

(2.) The neutral chromate and acetate of potash were diffused at a temperature ranging from 63° to 65°, or at a mean temperature of 64°·1, which almost coincides with the higher temperature of the last experiments.

Table VIII.—Diffusion of Chromate of Potash and Acetate of Potash, at 64°·1.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	Experiments.	Mean.
Chromate of potash.			
2	1·0158	5·79	
		5·66	
		5·86	5·77
4	1·0313	11·10	
		11·35	
		11·13	11·19
6⅔	1·0512	17·76	
		17·72	
		17·32	17·60
10	1·0750	24·49	
		24·92	
		24·85	24·75
Acetate of potash.			
2	1·0095	5·93	
		5·75	
		5·88	5·85
4	1·0184	10·55	
		10·56	
		10·98	10·70
6⅔	1·0306	16·53	
		16·06	
		16·84	16·48
10	1·0447	24·27	
		24·82	
		25·46	24·85

We have the same close correspondence in the diffusion products of these two salts as in the preceding group, and here the correspondence extends to the 10 per cent. solution.

Diffusion at 64°·1.

	2.	4.	6.	10.
Chromate of potash	5·77	11·19	17·60	24·75
Acetate of potash	5·85	10·70	16·48	24·85

The 10 per cent. solution of these two salts also agrees with the same solution of carbonate of potash, which was 24·69 grs. Nor do the lower proportions diverge greatly from the preceding group of salts.

(3). Another pair of salts were simultaneously diffused, but with an accidental difference of 0°·4 of temperature.

Table IX.—Diffusion of Bicarbonate of Potash, $KO.CO_2+HO.CO_2$, at 64°·1, and Bichromate of Potash, $KO.2CrO_3$, at 64°·5.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°·1 and 64°·5.	
		Experiments.	Mean.
Bicarbonate of potash.			
2	1·0129	5·74	
		5·77	
		5·91	5·81
4	1·0252	10·75	
		11·16	
		11·13	11·01
Bichromate of potash.			
2	1·0139	5·64	
		5·73	
		5·59	5·65
4	1·0273	11·55	
		11·54	
		11·39	11·49

Here again the two salts approach closely in diffusion, and also correspond well with the two preceding series.

Mean Diffusion at 64°·1 and 64°·5.

	2.	4.
Bicarbonate of potash	5·81	11·01
Bichromate of potash	5·65	11·49

It is singular to find that salts differing so much in constitution and atomic weight as the chromate and bichromate of potash, may be confounded in diffusibility. The diffusion products of these two salts are, for the 2 per cent. solutions, 5·77 and 5·65

grs., and for the 4 per cent. solution, 11·19 and 11·49 grs. The bicarbonate of potash also exhibits a considerable analogy to the carbonate, but resembles still more closely the acetate. It is thus obvious that equality, or similarity, of diffusion is not confined to the isomorphous groups of salts.

(4.) The nitrates of potash and ammonia have already appeared to be equidiffusive at two different temperatures. They were diffused again in the same proportions as the last salts, at a temperature varying from 63° to 67°·5.

TABLE X.—Diffusion of Nitrate of Potash and Nitrate of Ammonia at 65°·9.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	Experiments.	Mean.
Nitrate of potash.			
2	1·0123	7·34	
		7·58	
		7·49	7·47
4	1·0243	13·66	
		14·24	
		14·02	13·97
6⅔	1·0393	22·11	
		22·94	
		22·05	22·37
10	1·0581	32·06	
		32·90	
		32·50	32·49
Nitrate of ammonia, NH_4O, NO_5.			
2	1·0080	7·85	
		7·71	
		7·64	7·73
4	1·0154	14·20	
		14·79	
		14·45	14·48
6⅔	1·0256	23·66	
		23·35	
		22·22	22·74
10	1·0375	34·94	
		33·49	
		34·23	34·22

The solution of nitrate of ammonia of the water-jars was evaporated carefully at a temperature not exceeding 120° FAHR., to prevent loss of the salt by sublimation or decomposition.

Diffusion at 65°·9.

	2.	4.	6⅔.	10.
Nitrate of potash	7·47	13·97	22·37	32·49
Nitrate of ammonia	7·73	14·48	22·74	34·22

Although these salts correspond closely, it is probable that neither the diffusion of these nor the diffusion of any others is absolutely identical. The nitrate of ammonia appears to possess a slight superiority in diffusion over the nitrate of potash, which

increases with the large proportions of salt in solution. They are both considerably more diffusible than the seven preceding salts.

(5.) A second pair of isomorphous salts were compared, the chlorides of potassium and ammonium.

Table XI.—Diffusion of Chloride of Potassium and Chloride of Ammonium.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 66°·2.		At 64°·7.	
		Experiments.	Mean.	Experiments.	Mean.
Chloride of potassium.					
2	1·0127	7·83		8·03	
		7·72		7·89	7·96
		7·55	7·70		
4	1·0248	15·22		15·21	
		15·59		14·82	15·01
		15·07	15·29		
6⅔	1·0401	24·88		24·83	
		24·64		24·62	24·72
		25·09	24·87		
10	1·0592	36·23			
		37·63	36·93		
Chloride of ammonium.					
2	1·0061	7·10		7·10	
		8·52	7·81	7·24	7·17
4	1·0118	14·55		13·91	
		14·64	14·60	14·91	14·41
6⅔	1·0190	24·30	24·30	24·12	
				24·13	24·12
10	1·0272	36·53	36·53		

These two salts agree well in diffusibility, and are also evidently related to the preceding nitrates. The quantity of chloride of ammonium diffused was determined by evaporation, which is troublesome and may lead to small errors, from the volatility and efflorescent tendency of this salt. It would be easier and more accurate to determine this and other chlorides by the use of a normal solution of nitrate of silver, and so avoid evaporation.

Diffusion at 66°·2.

	2.	4.	6⅔.	10.
Chloride of potassium	7·70	15·29	24·87	36·93
Chloride of ammonium	7·81	14·60	24·30	36·53

The quantities diffused of these two chlorides are more closely in proportion to the strength of the original solution, than with any of the preceding salts of potash. Thus the quantities diffused from the 2 and 10 per cent. solutions of chloride of potassium are 7·70 and 36·93 grs., which are as 2 to 9·6, which is nearly as 2 to 10. Chloride of sodium was observed before to be nearly uniform in this respect; but other salts appear to lose considerably in diffusibility with the higher proportions of

salt. It is possibly a consequence of the crystallizing attraction, to which reference was lately made, coming into action in strong solutions and resisting diffusion.

(6.) The diffusion of chlorate of potash was observed at a temperature ranging from 63° to 65°, of which the mean was 64°·1.

TABLE XII.—Diffusion of Chlorate of Potash.

Parts of salt to 100 water.	Density of solution at 60°.	At 64°·1.	
		Experiments.	Mean.
2	1·0129	6·97	
		7·54	
		7·16	7·22
4	1·0246	13·03	
		13·64	
		13·27	13·31
6·5 (saturated solution).	1·0395	21·30	
		20·29	
		20·76	20·78

The solutions of chlorate of potash must be evaporated and the residuary salt dried at a temperature not exceeding 212°, otherwise a very sensible quantity of chloride of potassium may be formed. The chlorate appears to be sensibly inferior in diffusibility to the nitrate of potash. From the 4 per cent. solution of the chlorate we have a diffusion product of 13·27 grs., and from the corresponding solution of the nitrate 13·97 grs.; but the latter was obtained at a temperature 1°·8 higher than the former. It remains a question whether chlorate of potash does not really belong to the nitre group of salts, but has its diffusion interfered with by some secondary agency, such as its sparing solubility and consequent nearer approach to the saturating proportion.

It is certainly true that the uniformity of diffusion generally increases with the dilution of the solutions. This appears on comparing the diffusion of the 4 per cent. solution of what may be called the sulphate of potash group, with the diffusions of the 2 per cent. solutions of the same salts.

Diffusion of Salts of the Sulphate of Potash Class.

	4.	2.
Carbonate of potash	10·27	5·45
Sulphate of potash	10·57	5·52
Sulphate of ammonia.....	10·51	5·58
Acetate of potash	10·70	5·85
Bicarbonate of potash	11·01	5·81
Chromate of potash	11·19	5·77
Bichromate of potash	11·49	5·65

Thus while the 4 per cent. solutions range from 10·27 to 11·49 grs., or from 100 to 111·8, the 2 per cent. solutions range from 5·45 grs. to 5·85 grs., or from 100 to 107·3.

As it appeared to be in dilute solutions that the greatest uniformity of diffusion is to be expected, a series of experiments was instituted upon the preceding salts, with

the addition of acetate of potash, which appeared to belong to the same class, the solution employed being that of 1 salt to 100 water. The experiments were made in a vault, of which the temperature was nearly uniform, falling in a gradual manner from 59° to 58°, with a mean of 58°·5 during the period of seven days which the diffusion lasted. Eight phials of each salt were diffused, and the liquids of four water-jars evaporated together.

Carbonate of potash gave 10·42 and 10·59 grs. of salt diffused: mean 10·51 grs., or 2·63 grs. for one cell.

Sulphate of potash gave 10·72 and 10·78 grs. of salt diffused: mean 10·75 grs., or 2·69 grs. for one cell.

Acetate of potash, its diffusion product being treated with an excess of hydrochloric acid, gave 8·30 and 8·04 grs. of chloride of potassium, equivalent to 10·91 and 10·57 grs. of acetate of potash; mean 10·74 grs. of acetate of potash, or 2·68 grs. for one cell. The diffusion of these three salts is therefore remarkably similar:—

Diffusion of 1 *per cent. solutions at* 58°·5.

Carbonate of potash	2·63 grs.
Sulphate of potash	2·69 grs.
Acetate of potash	2·68 grs.

The 1 per cent. solution of neutral or yellow chromate of potash in good crystals gave 11·28 and 11·35 grs.; mean 11·31 grs., or 2·83 grs. for each cell. It was remarked of the diffused chromate in this experiment, that it contained a sensible quantity of green oxide of chromium. The diffusion of a salt appears indeed to try its tendencies to decomposition very severely.

The bicarbonate of potash gave 8·83 and 8·35 grs. of chloride of potassium, the diffusion product being neutralized with hydrochloric acid; equivalent to 11·25 and 11·21 grs. of bicarbonate of potash; mean 11·23 grs., or 2·81 grs. for one cell.

The bichromate of potash gave 11·54 and 11·49 grs. of salt diffused; mean 11·51 grs., or 2·88 grs. for one cell. These last three salts give all a larger diffusion product than the preceding three, while they agree well together. It is doubtful whether this excess in their diffusion is occasioned by a partial decomposition in the act of diffusion, which might be of such a kind as to increase the real or apparent diffusion in every one of them, or whether it is a peculiar character of this little group, to which the ferricyanide of potassium, it will be afterwards seen, falls to be added, while the ferrocyanide appears to belong to the other group:—

Diffusion of 1 *per cent. solutions at* 58°·5.

Chromate of potash	2·83 grs.
Bicarbonate of potash . . .	2·81 grs.
Bichromate of potash	2·88 grs.

The divergence from each other of two salts so closely isomorphous as sulphate and

chromate of potash, in the proportion of 100 to 105·2, is certainly remarkable, unless due to a slight decomposition of the latter.

(7.) *Ferrocyanide and Ferricyanide of Potassium.*

Of these two salts the 1 per cent. solution only was diffused. The time of diffusion was seven days, as usual; the mean temperature 54°·5. In evaporating the liquid of the water-jars, both salts were partially decomposed, so that it became necessary to estimate the diffusion product by a determination of the potash. Eight cells were employed for one salt and six for the other, and the liquids of the water-jars evaporated two together.

The diffusion product of ferrocyanide of potassium (anhydrous) was 5·02, 5·22, 5·02 and 5·20 grs.; mean 5·12 grs., or for one cell 2·56 grs.

The diffusion product of ferricyanide of potassium was 5·54, 5·64 and 5·36 grs.; mean 5·51 grs., or for one cell 2·75 grs.

Three cells of a similar solution of sulphate of potash which were diffused for seven days at a mean temperature 1° lower, or of 53°·5, gave 2·56, 2·53 and 2·62 grs.; mean for one cell 2·57 grs., a number which almost coincides with that of the ferrocyanide of potassium (2·56 grs.). The ferricyanide of potassium, on the other hand, is sensibly more diffusive, as 107·6 to 100, and appears to rank with the bicarbonate and bichromate of potash. The ferricyanide of potassium, again, is a salt which probably undergoes a slight decomposition in diffusion like those salts mentioned:—

Diffusion of 1 *per cent. solutions.*

Sulphate of potash	2·57 grs. at 53°·5.
Ferrocyanide of potassium . .	2·56 grs. at 54°·5.
Ferricyanide of potassium . .	2·75 grs. at 54°·5.

The salts of the nitre class may also be compared in the same manner, and I shall now add a third series of results obtained from the diffusion of 1 per cent. solutions of the same salts. The temperature of diffusion of this new series was 64°·5. Six phials of each salt were diffused, and they were evaporated afterwards two and two. This double diffusion product, however, is divided by 2 in the table.

Diffusion of Salts of the Nitre Class.

	4.	2.	1.
Nitrate of potash	13·97	7·47	3·72
Nitrate of ammonia	14·48	7·73	3·75
Chloride of potassium	15·01	7·70	3·88
Chloride of ammonium	14·41	7·81	3·89
Chlorate of potash.....	13·31	7·22	3·66
Mean	14·23	7·58	3·78

It is interesting to observe how the chlorate of potash rises in the lower proportions and approaches to the normal rate of its class. The diffusion products of all the salts are obviously more uniform for the two than for the 4 per cent. solutions, and again more uniform for the 1 than for the 2 per cent. solutions. The extremes in the 1 per cent. solutions are 3·66 grs. chlorate of potash, and 3·89 grs. chloride of ammonium, which are as 1 to 1·0628. We have here an approach to equality in diffusion, which appears to be as close as the experimental determinations are of the specific heat of different bodies belonging to one class. The numbers for the specific heat of equivalents of the metallic elements are known to vary as 38 to 42.

The salts of potash thus appear to fall into two groups of very similar if not equal diffusibility. What is the relation between these groups?

The diffusion of 4 per cent. solutions of carbonate and nitrate of potash was repeated at a temperature rising gradually from 63° to 65° during the seven days of the experiment, with a mean of 64°·1. The diffusion products of the carbonate were 10·31, 10·05 and 10·44 grs. in three cells; mean 10·27 grs. Of the nitrate, 13·98, 13·86 and 13·60 grs.; mean 13·81 grs. We have thus a diffusion in equal times of—

Carbonate of potash .	10·27	1
Nitrate of potash . .	13·81	1·3447

These experiments are almost identical with the former results, 10·25 carbonate of potash, and 13·97 nitrate of potash.

But the numbers thus obtained cannot be fairly compared, owing to the diminishing progression in which the diffusion of a salt takes place. Thus when the diffusion of nitrate of potash was interrupted every two days, as in a former experiment with chloride of sodium, the progress of the diffusion for eight days was found to be as follows in a 4 per cent. solution, with a mean temperature of 66°.

Nitrate of Potash.

Diffused in first two days	4·54 grs.
Diffused in second two days . . .	4·13 grs.
Diffused in third two days . . .	4·06 grs.
Diffused in fourth two days . . .	3·18 grs.
	15·91

The absence of uniformity in this progression is no doubt chiefly due to the want of geometrical regularity in the form of the neck and shoulder of the solution phial. A plain cylinder, as the solution cell, might give a more uniform progression, but would increase greatly the difficulties of manipulation.

The diffusion of carbonate of potash will no doubt follow a diminishing progression also; but there is this difference, that the latter salt will not advance so far in its progression, owing to its smaller diffusibility, in the seven days of the experiment, as the more diffusible nitrate does. The diffusion of the carbonate will thus be given

in excess, and as it is the smaller diffusion, the difference of the diffusion of the two salts will not be fully brought out.

The only way in which the comparison of the two salts can be made with perfect fairness, is to allow the diffusion of the slower salt to proceed for a longer time, till in fact the quantity diffused is the same for this as for the other salt, and the same point in the progression has therefore been obtained in both; and to note the time required. The problem takes the form of determining the times of equal diffusion of the two salts. This procedure is the more necessary from the inapplicability of calculation to the diffusion progression.

Further, allowing the Times of Equal Diffusion to be found, it is not to be expected that they will present a simple relation. Recurring to the analogy of gaseous diffusion, the times in which equal volumes or equal weights of two gases diffuse are as the square roots of the densities of the gases. The times, for instance, in which equal quantities of oxygen and hydrogen escape out of a vessel into the air, in similar circumstances, are as 4 to 1; the densities of these two gases as 16 to 1. Or, the times of equal diffusion of oxygen and protocarburetted hydrogen are as 1·4142 to 1, that is as the square root of 2 to the square root of 1; the densities of these gases being 16 and 8, which are as 2 to 1. The densities are the squares of the equal-diffusion times. It is not therefore the times themselves of equal diffusion of two salts, but the squares of those times which are likely to exhibit a simple relation.

(1.) While the 4 per cent. solution of nitrate of potash was diffused as usual for seven days, the corresponding solution of carbonate of potash was now allowed to diffuse for 9·90 days; times which are as 1 to 1·4142, or as 1 to the square root of 2.

The results were as follows: diffused of—

Nitrate of potash at 64°·1, in seven days, 13·81 grs. . . 100

Carbonate of potash at 64°·3, in 9·9 days, 13·92 grs. . . 100·8

The three experiments on the nitrate of potash, of which 13·81 grs. is the mean, were 13·98, 13·86 and 13·60 grs., as already detailed. The three experiments on the carbonate were 14·00, 13·97 and 13·78 grs. The difference in the means of the two salts is only 0·11 gr. The results appear to be as near to equality as could be reasonably expected from the method of experimenting. Seven and 9·90 may therefore be considered as the times of equal diffusion indicated for nitrate and carbonate of potash. The times of equal diffusion, or the diffusibilities of nitrate and carbonate of potash, would appear therefore to be in the proportion of the square root of 1 to the square root of 2.

The explanation of such a relation suggested by gaseous diffusion has been anticipated. It is that the two salts have different densities in solution, that of nitrate of potash being 1, and that of carbonate of potash 2. We are thus led to ascribe, what may be called Solution Densities, to the salts. The two salts in question are related exactly like protocarburetted hydrogen gas, of density 1, to oxygen gas of density 2. The parallel would be completed by supposing that the single volume of oxygen to

be diffused was previously mixed with 100 volumes of air (or any other diluting gas), while the 2 volumes of protocarburetted hydrogen were also diluted with 100 volumes of air; the diluting air here representing the water in which the salts to be diffused are dissolved in the solution cell. The time in which a certain quantity of protocarburetted hydrogen would come out from a vessel containing 1 per cent. of that gas being 1 (the square root of density 1), the time in which an equal quantity of oxygen would diffuse out from a similar vessel containing 1 per cent. also would be 1·4142 (the square root of density 2).

(2.) A solution of 4 parts of sulphate of potash in 100 water was diffused simultaneously with the last solution of carbonate of potash, and therefore in similar circumstances. The diffusion products of three experiments were 14·46, 14·21 and 14·53 grs.; mean 14·40 grs. This is in the proportion of 104·27 sulphate of potash to 100 nitrate of potash; so that the approximation to equality of diffusion with nitrate of potash, in the selected times, is not so close for the sulphate as for the carbonate of potash.

(3.) The diffusion was repeated of 2 per cent. solutions of the nitrate and carbonate of potash at a lower temperature by about 10°. The temperature of the solutions was rather unsteady; ranging from 56° to 52°·25 for the first period of seven days, from 56° to 50°·5 for the period of 9·90 days, and from 55° to 50°·5 for a second period of seven days; the external atmospheric temperature having fallen during the same period more than 20 degrees. Six phials of each solution were diffused and evaporated two together; so that the results are all double quantities.

At a mean temperature of 54°·3, the nitrate of potash gave in seven days 12·60 and 12·13 grs.; mean 12·36 grs.

Again, at a mean temperature of 52°·4, the nitrate of potash gave in seven days 11·85, 12·40 and 11·95 grs.; mean 12·06 grs.

The carbonate of potash gave in 9·90 days, with a mean temperature of 53°·4, 12·69, 12·40 and 12·12 grs.; mean 12·40 grs.

The general results are—

Nitrate of potash, in seven days, at 54°·3 .	12·36 grs.
Carbonate of potash, in 9·9 days, at 53°·4 .	12·40 grs.
Nitrate of potash, in seven days, at 52°·4 .	12·06 grs.

As the first nitrate is 0°·9 above the carbonate and the second nitrate 1° below it, we may take the mean of the two nitrates as corresponding to the temperature of the carbonate. We thus finally obtain, diffused at 53°·4, of—

Nitrate of potash in seven days, 12·22 grs. . .	100
Carbonate of potash in 9·9 days, 12·40 grs. . .	101·47

The difference in the amount of the diffusion of the two salts in these times is only 0·18 gr., or 1½ per cent.

These last experiments may be held therefore as tending to the same conclusion as

the former series, although the circumstances were more than usually unfavourable to their success. To find whether the same relation existed between the salts through a considerable range of temperature, an opportunity was taken during cold weather to repeat the experiments at a low temperature.

(4.) Solutions of 1 salt in 100 water were diffused from eight solution cells, for each salt. The times were increased, but the same ratio of 1 to 1·4142 was preserved between them. The liquids of the cells were found to retain a temperature ranging slowly between 41° and 38°·8 during the whole period of the observations. Sulphate of potash was substituted for the carbonate, as of these two equi-diffusive salts the former had been found to be least in accordance with nitrate of potash, in the 4 per cent. solutions, and appeared therefore to afford the severest test of the relation.

For nitrate of potash, at a mean temperature of 39°·7, during nine days, the diffusion product of two cells together was 6·97, 6·93, 6·77 and 6·64 grs.; mean 6·83 grs. for two cells.

For sulphate of potash, at the same mean temperature of 39°·7, during 12·728 days (twelve days, seventeen hours, twenty-eight minutes), the diffusion product of two cells together was 7·05, 6·93, 7·28 and 6·90 grs.; mean 7·04 grs. for two cells.

The general results are—

Nitrate of potash in nine days at 39°·7 . .	6·83 grs. . .	100
Sulphate of potash in 12·728 days at 39°·7	7·04 grs. . .	103·07

(5.) Solutions of 2 salt in 100 water were diffused simultaneously with the preceding experiments, and in precisely the same conditions of time and temperature.

The diffusion product of nitrate of potash during nine days, at a mean temperature of 39°·7, was 7·03, 6·63, 6·83 and 6·83 grs. for one cell; mean 6·83 grs. for one cell, or the same number as for two cells with the 1 per cent. solution.

The diffusion product of sulphate of potash during 12·728 days was 6·84, and 6·80; mean 6·82 grs. for one cell. These experiments almost coincide with the number for nitrate of potash.

Nitrate of potash, 6·83 grs.	100
Sulphate of potash, 6·82 grs.	99·85

(6.) The existence of the relation in question was also severely tested in another manner. Preserving the ratio in the times of diffusion for the two salts, the actual times were varied in duration, in three series of experiments, as 1, 2 and 3. The experiments were made in the vault, with a uniformity of temperature favourable to accuracy of observation. Eight cells of the 1 per cent. solution of each salt were always diffused at the same time.

(*a*.) Nitrate of potash diffused for 3·5 days, at 47°·2, gave for two cells, 3·55, 3·63, 3·33 and 3·51 grs.; mean for two cells, 3·50 grs.

Sulphate of potash diffused for 4·95 days, at 47°·3, gave for two cells, 3·54, 3·31,

3·51 and 3·63 grs.; mean for two cells, 3·50 grs., or exactly the same as for nitrate of potash above.

(*b.*) Nitrate of potash diffused for seven days, at 48°·6, gave 6·1, 6·2, 5·9 and 5·92 grs.; mean for two cells, 6·04 grs.

Sulphate of potash diffused for 9·9 days, at 49°·1, gave 6·13, 5·92, 6·18 and 6·59 grs.; mean 6·20 grs., or, excluding the last experiment, 6·08 grs.

Chromate of potash diffused also for 9·9 days, at 49°·1, gave 6·19, 6·18, 6·40 and 6·38 grs.; mean for two cells, 6·29 grs. The diffused chromate presented no appearance of decomposition on this occasion.

(*c.*) Nitrate of potash diffused for 10·5 days, at 48°, gave 8·36, 8·95, 8·82 and 8·84 grs.; mean for two cells, 8·74 grs.

Sulphate of potash diffused for 14·85 days, at 48° 6, gave 8·99, 8·94, 8·66 and 8·56 grs.; mean for two cells, 8·79 grs.

The mean results for the three different sets of periods of diffusion are as follows:—

3·5 and 4·95 days	Nitrate of potash, at 47°·2, 3·50 grs. . . .	100
	Sulphate of potash, at 47°·3, 3·50 grs. . . .	100
7 and 9·9 days	Nitrate of potash, at 48°·6, 6·04 grs. . . .	100
	Sulphate of potash, at 49°·1, 6·20 grs. . . .	102·65
	Chromate of potash, at 49°·1, 6·29 grs. . .	104·14
10·5 and 14·85 days	Nitrate of potash, at 48°, 8·74 grs.	100
	Sulphate of potash, at 48°·6, 8·79 grs. . . .	100·57

The concurring evidence of these three series of experiments appears to be quite decisive in favour of the assumed relation of 1 to 1·4142, between the times of equal diffusion for the nitrate and sulphate of potash, and consequently of the times for the two classes of potash salts, of which the salts named are types. The same experiments are also valuable as proving the similarity of the progression of diffusion, in two salts of unequal diffusibility. I shall return again to the relation between nitrates and sulphates, under the salts of soda.

(8.) *Hydrate of Potash.*

(1.) Eight cells of the 1 per cent. solution of pure fused hydrate of potash were diffused for seven days in the vault, with a temperature ranging only from 59° to 58°, of which the mean was 58°·6. The product of four cells evaporated together was 17·57 grs. of hydrate of potash, and of the other four cells 17·19 grs.; mean 17·38 grs., or 4·345 grs. for one cell. The hydrate of potash was estimated from the chloride of potassium which it gave when saturated with hydrochloric acid. The diffusion product of sulphate of potash for seven days, at 58°·5, or almost the same temperature, was 10·75 grs. for the four cells, as already stated, and consequently 2·64 grs. for one cell. It thus appears that the hydrate of potash is greatly more diffusive than the sulphate of potash in the same period of seven days, namely, as 4·345 to 2·64.

Such a result indeed is not inconsistent with the times of equal diffusion of these two substances, differing as much as 1 to 2.

(2.) Of pure fused hydrate of potash, a 1 per cent. solution was diffused from four cells for 4·95 days at a mean temperature of 53°·7, against a 1 per cent. solution of nitrate of potash in six cells, for seven days, at a mean temperature 0°·1 lower, or of 53°·6. The hydrate of potash which diffused, is calculated as before from the chloride of potassium which it gave, when neutralized by hydrochloric acid. Hydrate of potash diffused from two cells 5·97 and 6·28 grs.; mean 6·12 grs., or 3·06 grs. for a single cell.

Nitrate of potash diffused from two cells 6·22, 6·54 and 5·93 grs; mean 6·23 grs., or 3·11 grs. for a single cell. The diffusion of nitrate of potash being 100, that of the hydrate of potash is 98·2, numbers which are sufficiently in accordance. But the times were as 1 to 1·4142, and their squares as 1 to 2. So far then as this series of experiments on hydrate of potash entitles us to conclude, we appear to have for the salts of potash a close approximation to the following simple series of squares of equal diffusion times:—

Squares of Times of Equal Diffusion, or Solution Densities.

Hydrate of potash	1
Nitrate of potash	2
Sulphate of potash	4

(3.) The hydrate of potash was also diffused at the lower temperature, 39°·7, in company with the nitrate and sulphate of potash for a period of 6·364 days (six days, eight hours, forty-four minutes).

The 1 per cent. solution of hydrate of potash gave in eight cells, evaporated two together, 6·93, 6·93, 6·93 and 6·89 grs.; mean 6·92 grs.

The 2 per cent. solution of hydrate of potash gave in three single cells, 6·77, 6·49 and 7·10 grs.; mean 6·79 grs.

The diffusion of nitrate of potash in nine days at the same temperature, as already detailed, was sensibly the same, or 6·83 grs. for both the 1 and 2 per cent. solutions. The times for the two salts were as 1 to 1·4142.

The diffusion of hydrate of potash, at 39°·7, may therefore be stated with reference to that of nitrate of potash, for the selected times, as follows:—

Nitrate of potash, 1 and 2 per cent. solutions.	100
Hydrate of potash, 1 per cent. solution.	101·3
Hydrate of potash, 2 per cent. solution	99·4

These experiments at the low temperature concur, therefore, with those made at the higher temperature, in proving that the times of equal diffusion of the two substances have been properly chosen.

III. DIFFUSION OF SALTS OF SODA.

(1.) The only salts of soda which I have yet had an opportunity of diffusing in a sufficient variety of circumstances are the carbonate and sulphate. These salts appear to be equi-diffusive, but to diverge notwithstanding more widely in the solutions of the higher proportions of salt than the corresponding potash salts. It is a question whether this increased divergence is not due to the less solubility of the soda salts, and the nearer approach consequently to their points of saturation in the stronger solutions.

TABLE XIII.—Diffusion of Carbonate and Sulphate of Soda.

Parts of anhydrous salt to 100 water.	Density of solution at 60°.	At 64°.		At 37°·7.	
		Experiments.	Mean.	Experiments.	Mean.
Carbonate of soda.					
2	1·0202	4·15		2·78	
		4·08		2·62	
		4·21	4·14	2·73	2·71
4	1·0405	7·96		5·31	
		7·70		4·94	
		7·68	7·78	5·35	5·20
6⅔	1·0653	12·16		8·50	
		12·06		8·45	
		12·45	12·22	8·05	8·33
10	1·0957	17·13			
		16·53			
		17·00	16·88		
Sulphate of soda.					
2	1·0179	4·35		2·96	
		4·32		3·03	
		4·25	4·31	3·09	3·03
4	1·0352	8·14		5·63	
		8·10		5·64	
		8·28	8·17	5·42	5·56
6⅔	1·0578	13·26		8·77	
		13·63		8·84	8·80
		13·61	13·50		
10	1·0847	18·71			
		19·73			
		18·91	19·14		

The range of the thermometer during the continuance of the experiments at the higher temperature was from 64°·5 up to 65° and falling again to 63°; the mean of all the days being 64°. The temperature of the other series, or of the ice-box, was 42° the first day, 38° the second, and 37° steadily for the remainder of the period; the mean being 37°·7.

The mean results at 64° are as follows:—

	2.	4.	6⅔.	10.
Carbonate of soda	4·14	7·78	12·22	16·88
Sulphate of soda	4·31	8·17	13·50	19·14

Another series of experiments was made upon a 1 per cent. solution of the same salts at a mean temperature of 64°·9. Six phials of each solution were diffused, and the water of two jars afterwards evaporated together, so that the quantities stated are double.

The diffusion product in three experiments with the sulphate of soda was 4·77, 4·75 and 4·80 grs.; mean 4·77 grs. The diffusion product in three experiments with the carbonate of soda was 4·61, 4·68 and 4·67 grs.; mean 4·65 grs. The difference between the carbonate and sulphate is 0·12 gr.; it is less for the present proportion of 1 per cent. of salt, than for 2 per cent., so that the diffusion of the salts may be converging to a perfect equality in very weak solutions. One-half of the preceding quantities, or the mean results for a single diffusion cell, are—

Diffusion of 1 *per cent. solutions at* 64°·9.

Carbonate of soda, 2·32 grs.	100
Sulphate of soda, 2·38 grs.	102·58

(2.) The diffusion of the carbonate of soda was further compared with the nitrate of the same base, to find whether their times of equal diffusion are related like those of the corresponding potash salts. The mean temperature of the first seven days, which was the period of diffusion for the nitrate of soda, was 66°·9; of the last three days, 65°·2; and of the whole period of 9·9 days occupied by the carbonate of soda, 66°·4. The 4 per cent. solutions were employed.

The nitrate of soda gave a diffusion product, in three experiments, of 11·48, 11·58 and 12·13 grs.; mean 11·73 grs.

The carbonate of soda, in three experiments, gave 11·66, 11·53 and 11·52 grs.; mean 11·57 grs. A slight addition should be made to the latter quantity to raise the diffusion product from 66°·4 to 66°·9. It will appear from a subsequent experiment that the diffusion of the carbonate of soda increases 0·096 gr. for a rise of one degree of temperature; which will give 0·05 gr. for the half degree in question. Bringing the diffusion of the two salts to the same temperature of 66°·9, we have therefore diffused, of—

Nitrate of soda, in seven days, 11·73 grs.	100
Carbonate of soda, in 9·9 days, 11·62 grs.	99·06

The difference in the quantity diffused of the two salts is only 0·11 gr., or 1 per cent., which is quite within the unavoidable errors of observation.

(3.) The diffusion of a 2 per cent. solution of the same salts was repeated at the same inferior temperature of 54°·3 as with the salts of potash, and under the same difficulties from fluctuation of atmospheric temperature. Two water-jars were evaporated together, so that the results are double.

Nitrate of soda, diffused for seven days at a mean temperature of 54°·3, gave 10·15, 10·24 and 9·92 grs. in three experiments; mean 10·10 grs.

Carbonate of soda, diffused for 9·9 days at a mean temperature of 53°·4, gave 9·93, 9·54 and 10·10 grs. in three experiments; mean 9·86 grs. But the latter amount is to be increased by 0·09 gr. to bring it to the diffusion of 54°·3. We have then for the diffusion product of the two salts at the same temperature of 54°·3—

Nitrate of soda, in 7 days, 10·10 grs. 100
Carbonate of soda, in 9·9 days, 9·95 grs. . . . 98·51

The difference is again small, namely, 0·15 gr., or $1\frac{1}{2}$ per cent., and within the limits of unavoidable error.

It appears therefore that the times of equal diffusion of the nitrate and carbonate of soda are related like those of the nitrate and carbonate of potash, or as the square root of 1 and 2, that is, as 1 to 1·4142.

Relation of Salts of Potash to Salts of Soda.

It appeared probable, from many of the experiments already recorded, that if any relation, in the times of equal diffusibility, existed between the corresponding salts of potash and soda, it was that of the square root of 2 to the square root of 3. They were accordingly diffused for times having this ratio; namely, the nitrate of potash for seven days, the nitrate of soda for 8·57325 days; the sulphate and carbonate of potash for 9·9 days, and the sulphate and carbonate of soda for 12·125 days. If these times are rightly chosen, the eventual diffusion products of all the experiments should be equal. The 1 per cent. solution was selected, and the number of experiments simultaneously made on each salt was eight or six. The liquids of two water-jars were evaporated together, so that each of the results in the table below represents the diffusion of two cells. These experiments also afford another opportunity of testing the assumed relation between the nitrates and sulphates of the same base.

Table XIV.—Solution: 1 Salt to 100 Water, at 55°·4—56°·1.

	Temperature.	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in grs.				
				Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Nitrate of potash	56°·1	7	2	6·67	6·87	6·90	6·57	6·75
Nitrate of soda	55·7	8·57	3	6·59	6·80	6·94	6·57	6·78
Sulphate of potash.....	55·4	9·90	4	6·73	6·77	6·96	6·68	6·78
Sulphate of soda	55·4	12·125	6	6·43	6·94	6·80	6·68	6 72
Carbonate of potash	55·4	9·90	4	6·54	6·64	6·40	6·67	6·56
Carbonate of soda	55·4	12·125	6	6·40	6·63	6·60	6·67	6·54

The range of temperature during the period of these experiments rather exceeded 3 degrees, so that they cannot be considered as fortunate in that respect; but still the similarity between the different sets of experiments, and the near equality of their means, is very remarkable. The two nitrates and the two sulphates may be said to coincide, the extreme difference of the means of the four salts not being quite so much as 1 per cent. The two carbonates fall about 3·4 per cent. below the sul-

phates and nitrates, but agree perfectly with each other, showing a uniformity in their irregularity. This deviation of the carbonates would appear essential, as it has been observed every time they have been compared with the sulphates.

The double relation between salts of potash and salts of soda, and between the nitrate and sulphate class of each of these bases, will, I believe, be allowed to acquire considerable additional support from this new series of observations.

IV. DIFFUSION OF SULPHATE OF MAGNESIA.

In a set of preliminary experiments upon sulphate of magnesia in comparison with sulphate of potash, the 4 per cent. solutions of both salts were diffused for seven days at a mean temperature of 57°·9, with very little fluctuation, the extreme range being from 58°·5 to 57°·75. The sulphate of magnesia is taken anhydrous in all the following experiments. The diffusion of sulphate of potash in three cells was 9·16, 9·22 and 9·57 grs.; mean 9·32 grs.

The diffusion of sulphate of magnesia in three cells was 5·21, 4·98 and 5·34 grs.; mean 5·18 grs. The diffusion, in equal times, appears here to be as 100 sulphate of potash to 55·58 sulphate of magnesia. We know, however, when unequally diffusible salts are diffused for equal times, that the diffusion of the slower is exaggerated. Consequently the diffusion of sulphate of magnesia is likely to be represented in excess in these experiments.

In a second preliminary series of experiments the same 4 per cent. solutions were diffused, the sulphate of potash for eight days and the sulphate of magnesia for nineteen days, with the view of discovering their times of equal diffusibility.

During the first period of eight days the temperature fluctuated considerably, beginning at 54°, falling gradually in four days to 50°·5, and rising again in four days to 53°; the average of the whole period was 52°·2. The diffusion of sulphate of potash from three cells was 9·36, 9·25 and 10·52 grs.; mean 9·71 grs.

During the second period of nineteen days, which included the first period, the mean temperature was 54°·6. The diffusion of sulphate of magnesia from three cells was 11·81, 11·61 and 10·90 grs.; mean 11·44 grs. The variation in the amounts diffused of both salts is greater than usual, owing no doubt to the changes of temperature, which were imperfectly controlled.

Dividing the quantity of salt diffused by the number of days, we have of sulphate of potash 1·214 gr. diffused per day, and of sulphate of magnesia 0·602 gr. per day; or the latter salt exhibits sensibly half the diffusibility of the former in equal times. This suggested the trial of times for these two salts in the proportion of 1 to 2, with the view of obtaining equal diffusions.

(1.) A one per cent. solution of sulphate of magnesia (anhydrous) was diffused for the long period of 19·8 days, at a mean temperature of 54°·7, in eight cells. The diffusion products of four pairs of cells were 7·07, 6·71, 7·07 and 7·35 grs.; mean 7·05 grs., or for one cell, 3·53 grs.

A similar solution of sulphate of potash diffused for 9·9 days, or half the preceding period, at a mean temperature of 55°·4, or 0°·7 higher, gave a mean product, for two cells, of 6·79 grs., as before stated, or for one cell, of 3·40 grs. The diffusion of sulphate of potash being 100, that of sulphate of magnesia is therefore 103·7, a fair approximation to equality.

(2.) In a second series of experiments upon 1 per cent. solutions of the same two salts, diffused in the vault for fourteen and seven days respectively, with a mean temperature of 53°·8 for the sulphate of magnesia, and 54°·3 for the sulphate of potash, the temperature was remarkably uniform, gradually falling from 55°·2 to 53° during the longer period, but without any injurious oscillation.

From eight cells, evaporated two together, the sulphate of magnesia obtained was 6·12, 6·12, 6·04 and 6·03 grs.; mean 6·08 grs., or 3·04 grs. for one cell.

The sulphate of potash gave from eight cells, in experiments already detailed, a mean result of 5·84 grs. of salt for two cells, or 2·92 grs. for one cell. The diffusion is in the proportion of 100 sulphate of potash to 104·11 sulphate of magnesia, the times being as 1 to 2 for the two salts respectively.

From these two series of experiments, it appears that, at 54°, sulphate of magnesia has nearly, if not exactly, half the diffusibility of sulphate of potash, and consequently one-fourth of that of hydrate of potash. Or, the times of equal diffusion for these three salts appear to be 1, 2 and 4. The squares of these times and the solution densities are 1, 4 and 16. Hydrate of potash may possibly therefore have the same relation to sulphate of magnesia in solution density and diffusibility that hydrogen gas has to oxygen gas.

(3.) A two per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at 53°·9, for two pairs of cells, 9·57 and 10·00 grs. of salt, of which the mean is 9·79 grs., or 4·85 grs. for one cell.

A similar solution of sulphate of potash diffused for seven days gave a mean result of 4·97 grs. of salt for one cell, at 54°·2, as already stated. The result is a diffusion of 100 sulphate of potash to 97·59 sulphate of magnesia.

(4.) A four per cent. solution of sulphate of magnesia, diffused for fourteen days, gave at 53°·7, in two pairs of cells, 18·00 and 18·20 grs. of salt; mean 18·10 grs. for two cells, or 9·05 grs. for a single cell.

A similar solution of sulphate of potash, diffused for seven days at 54°·2, gave a mean result of 9·30 grs. of salt for a single cell, as already stated. This is a diffusion of 100 sulphate of potash to 97·4 sulphate of magnesia.

The diffusion of the 2 and 4 per cent. solutions of sulphate of magnesia is so nearly equal to the diffusion of the same proportions of sulphate of potash in half the time, that they may be considered as supplying additional support to the assumed relation between the diffusibilities of these salts.

I may add, that a 4 per cent. solution of anhydrous sulphate of zinc was diffused for fourteen days, simultaneously with the similar solution of sulphate of magnesia,

and of course at the same temperature of 53°·7. Two cells, evaporated two together, gave 17·40 and 17·36 grs. of ignited sulphate of zinc; mean 17·38 grs. The salt remained, after ignition, entirely soluble. This is a diffusion of 8·69 grs. for one cell, while the sulphate of magnesia gave 9·05 grs.; or of 100 sulphate of zinc to 104·14 sulphate of magnesia. This result is interesting, as we here find two salts which are isomorphous, and of which the equi-diffusion is on that account in a high degree probable, differing between themselves so much as 4 per cent.

Another numerous series of experiments was made at a considerably lower temperature, with the view of testing several of the same relations. The temperature in commencing the diffusion was 41°, but fell in the course of three days to 38°·8, and afterwards rose to 39°, from which it never varied afterwards more than a degree during the diffusion of the salts of potash and soda. The mean temperature for their periods did not vary above 0°·1 or 0°·2 from 39°·7, so that it may be supposed the same for all these salts. For the sulphates of magnesia, the mean temperature was 38°·9, or 0°·8 lower. The times chosen are as the square-roots of 2, 3, 6 and 16.

TABLE XV.—Solutions of 1 and 2 Salt to 100 Water, at 39°·7.

	Time in days.	Square of times. Sol. density.	Diffusion product of two cells in 1 per cent. solutions, and one cell in 2 per cent. solutions.				
			Exp. I.	Exp. II.	Exp. III.	Exp. IV.	Mean.
Chloride of potassium, 2 per cent....	9	2	6·58	6·79	6·82	.....	6·73
Nitrate of soda, 2 per cent.	11·022	3	6·66	6·98	6·79	.....	6·81
Chloride of sodium, 1 per cent. ...	11·022	3	6·33	6·63	6·73	7·06	6·69
Chloride of sodium, 2 per cent. ...	11·022	3	6·50	6·60	6·64	6·74	6·62
Sulphate of soda, 1 per cent.....	15·589	6	6·60	6·56	6·56	6·50	6·55
Sulphate of soda, 2 per cent.....	15·589	6	6·50	5·43	6·33	.....	6·42
Sulphate of magnesia, 1 per cent....	25·456	16	6·36	6·20	6·86	6·59	6·50
Sulphate of magnesia, 2 per cent....	25·456	16	6·42	6·78	6·50	6·84	6·63

Several other salts were diffused in the same circumstances as the preceding, of which the diffusion products have been previously given. Of these salts, both the 1 and 2 per cent. solutions of nitrate of potash gave 6·83 in nine days, or in the same time as chloride of potassium in the table. The latter salt maintains a sensible equality of diffusion with the present series at the low, as well as it was found to do at the former high temperature. Chloride of sodium is here introduced for the first time: it appears to be equi-diffusive with nitrate of soda. If the sulphate of magnesia diffused be increased by 0·07, for its lower temperature, this salt will be in close accordance with the salts of potash and soda.

Taking nitrate of potash 6·83, as 100, for a standard, the salt which deviates most considerably is sulphate of soda, which for the 1 per cent. solution is 6·55, or 95·9. A low temperature, however, must be unfavourable to diffusion experiments, from increasing the tendency of salts to crystallize.

In conclusion, I may sum up the results of most interest which this inquiry respecting liquid diffusion has hitherto furnished.

1. I would place first the method of observing liquid diffusion. This method, although simple, appears to admit of sufficient exactness. It enables us to make a new class of observations which can be expressed in numbers, and of which a vast variety of substances may be the object, in fact everything soluble. Diffusion is also a property of a fundamental character, upon which other properties depend, like the volatility of substances; while the number of substances which are soluble and therefore diffusible, appears to be much greater than the number of volatile bodies.

2. The novel scale of Solution Densities, which are suggested by the different diffusibilities of salts, and to which alone, guided by the analogy of gaseous diffusion, we can refer these diffusibilities. Liquid diffusion thus supplies the densities of a new kind of molecules, but nothing more respecting them.

The fact that the relations in diffusion of different substances refer to equal weights of those substances, and not to their atomic weights or equivalents, is one which reaches to the very basis of molecular chemistry. The relation most frequently possessed is that of equality, the relation of all others most easily observed. In liquid diffusion we appear to deal no longer with chemical equivalents or the Daltonian atoms, but with masses even more simply related to each other in weight. Founding still upon the chemical atoms, we may suppose that they can group together in such numbers as to form new and larger molecules of equal weight for different substances, or if not of equal weight, of weights which appear to have a simple relation to each other. It is this new class of molecules which appear to play a part in solubility and liquid diffusion, and not the atoms of chemical combination.

3. The formation of classes of equi-diffusive substances. These classes are evidently often more comprehensive than the isomorphous groups, although I have reason to imagine that they sometimes divide such groups; that while the diffusion of salts of baryta and strontia, for instance, is similar, the diffusion of salts of lead may be different.

4. The separation of the whole salts (apparently) of potash and of soda into two divisions, the sulphate and nitrate groups, which must have a chemical significancy. The same division of the salts in question has been made by M. Gerhardt, on the ground that the nitrate class is monobasic and the sulphate class bibasic.

5. The application of liquid diffusion to the separation of mixed salts, in natural and in artificial operations.

6. The application of liquid diffusion to produce chemical decompositions.

7. The assistance which a knowledge of liquid diffusion will afford in the investigation of endosmose. When the diffusibility of the salts in a liquid is known, the compound effect presented in an endosmotic experiment may be analysed, and the true share of the membrane in the result be ascertained.

But on the mere threshold of so wide a subject as liquid diffusion, I must postpone speculation to the determination of new facts and the enlargement of my data, of the present incompleteness of which I am fully sensible.

II. *On the Nitrogenated Principles of Vegetables as the Sources of Artificial Alkaloids.*

By Dr. John Stenhouse, *F.R.S.*

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Part I.

THERE are few departments in organic chemistry which during the last six or seven years have attracted more of the attention of experimenters than the artificial formation of the alkaloids. This perhaps is not to be wondered at when we consider the interesting nature of this class of bodies, both as regards their well-defined chemical properties and the important medical virtues which many of them possess. All attempts to form the natural alkaloids, such as quinine, cinchonine, strychnine, &c., by artificial means have hitherto been unsuccessful, but chemists have been enabled by various processes to procure artificially a considerable number of true alkaloids quite analogous to those which occur in nature. Several of these artificial alkaloids, such as quinoline, narcogenine, cotarnine, &c., are obtained from the natural alkaloids by acting on them by various reagents.

A second group, comprising furfurine, thiosinnamine, &c., are formed when ammonia is brought in contact with some of the essential oils, such as oil of mustard.

A third very numerous group, comprising nitraniline, toluidine, cumedine, &c., are obtained by the reducing action of sulphuretted hydrogen or sulphide of ammonium on nitrogenous compounds formed by treating certain hydrocarbons with nitric acid.

I shall conclude this enumeration by noticing a fourth very important group, comprising aniline, picoline, petenine, &c., which are obtained by the distillation of coal or animal substances, as in the case of bone-oil in the preparation of animal charcoal. To this last group I shall especially refer in the course of the present notice.

It is somewhat remarkable therefore, that while so many other sources have been examined, no attempt, so far as I am aware, should hitherto have been made to procure alkaloids from the highly nitrogenated principles, which under the names of vegetable albumen, fibrine, caseine, &c. are found in all plants, in many instances to a very considerable amount. These principles are, as is well known, almost as rich in nitrogen as the corresponding animal compounds, containing on an average about 15 per cent. of that element. What also renders the neglect of these substances by experiments still more singular, is the consideration that among the known sources of the artificial alkaloids coal has been one of the most productive, yielding as it does, in addition to ammonia, four other bases, aniline, quinoline, picoline and pyrrol, and not improbably containing also other organic bases which have hitherto escaped

observation. Now coal is universally admitted to be exclusively of vegetable origin, and to consist of the remains of a variety of vegetables, which, after having undergone putrefactive fermentation, and been subjected to probably enormous compression, have lain for countless ages in the bowels of the earth.

When reflecting therefore on the probable sources of the organic bases in coal, it has for some time past appeared to me highly probable that they are not derived from the woody fibre and other non-nitrogenated vegetable matters from which the coal has been principally formed; but that these bases are exclusively derived from the highly nitrogenated principles, previously enumerated, contained in the plants of the coal-fields. From the energetic agencies to which coal has been subjected, it seemed probable that much of the nitrogen originally present in the vegetables from which it has been formed must have been dissipated, and consequently the amount of bases now obtainable from coal proportionally diminished. It appeared therefore only reasonable to expect, that by acting on the nitrogenated principles of recent vegetables, the same organic bases as those contained in coal, or at any rate a series of analogous bases, would be obtained in proportionally greater abundance. In the sequel it will appear that this latter expectation has not been altogether disappointed.

It is extremely difficult to obtain vegetable albumen, fibrine, or caseine in considerable quantity in a state of purity. And though several chemists have bestowed much attention on the subject, as none of these principles are crystallizable, it is very doubtful if any of them have yet been obtained in a state of absolute purity. Instead therefore of endeavouring to purify these principles, I contented myself with selecting those portions of our commonest plants, usually their seeds, which contain them in the greatest abundance.

The first substance on which I operated was the seeds of the *Phaseolus communis*, or common horse-bean. This bean contains about 20·8 per cent. of caseine and 1·35 per cent. of albumen, amounting in all to a little more than 22 per cent. nitrogenous matter. The beans were destructively distilled in cast-iron cylinders, about three feet high and eight inches in diameter. The products of the distillation were collected by means of a large condensing Liebig's apparatus, kept carefully cool. A great deal of combustible but non-condensable gas was evolved. It had a very disagreeable fœtid odour. The liquid which passed into the receiver was strongly alkaline, so much so as to require about a third of its bulk of muriatic acid of ordinary strength to neutralize it. It closely resembled the products of the distillation of bones, flesh and other animal matters, being very complex, and comprising, among other substances, acetone, wood-spirit, acetic acid, empyreumatic oils, tar, a great deal of ammonia, and several organic bases. The crude produce of the distillation was then treated with a considerable excess of muriatic acid, and the clear liquid, after subsidence, was poured off from the tar and other empyreumatic matters which had fallen to the bottom of the vessel. The tarry residue was also repeatedly agitated with small quantities of water, so long as any bases appeared to be dis-

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solved. The several liquors were then mixed together, and were boiled for a couple of hours in a copper pan, or still more conveniently in an iron pot lined with enamel. This dissipated the acetone, wood-spirit, and a great deal of the neutral and acid empyreumatic volatile oils contained in the liquid. The boiling also rendered the tar less soluble by converting it and the fixed oils into imperfect resins. The acid liquor was then left at rest till it was quite cold, when it was passed through a cloth filter containing a quantity of pounded charcoal, which retained the greater portion of the resinous matter. The clear liquid was then introduced into a capacious still, and largely supersaturated either with quick-lime in fine powder, or with carbonate of soda, as was found most convenient.

As soon as heat was applied to the still a great deal of ammonia was evolved, and when the liquid boiled a quantity of oily bases began to appear in the ammoniacal liquor which passed into the receiver. Their amount increased as the distillation proceeded. As the first half of the liquid which came over was by much the richest in bases, it was collected separately from the succeeding portions, which contained scarcely any undissolved oil, but consisted chiefly of an aqueous solution of the bases. The distillation was continued however till the liquid which condensed in the receiver had only a slightly alkaline reaction. The mixture of oils which collected on the surface of the first portion of the distillation was drawn off with a pipette and then saturated with muriatic acid, which left any neutral oil which had been mixed with it undissolved. The oil was removed by passing the solution through a wet paper filter. The clear liquid was next supersaturated with carbonate of soda, and rectified in a large glass retort. It was found advantageous to employ a great excess of alkali for this purpose, as these bases are much more soluble in water than in strong alkaline lyes, and therefore distil over more readily from solutions which are strongly alkaline. The bases which passed over into the receiver were drawn off, as before, by means of a pipette from the ammoniacal liquor on which they floated, and were collected in any suitable bottle. The weak alkaline liquors of the previous distillation, which had ceased to yield bases by simple rectification, were again neutralized with muriatic acid, and cautiously concentrated to about half, or even a third, of their bulk, according to their state of dilution. Care should be taken however not to concentrate these liquors, unless in case of necessity, as long-continued boiling has always the effect of destroying a large portion of the bases, which are oxidated and converted into dark-coloured resins. The bases were again rectified with water, which removed much of the resinous matter which had come over with them during the previous distillations. As they still however retained a good deal of ammonia, from which it was necessary to free them, they were washed by being repeatedly agitated with successive portions of a strong solution of potash, which dissolved the ammonia and retained it in solution. The mixture of the lye and the bases was then poured into a long narrow-necked funnel, which was closed at the bottom, and the whole was left for a short time to subside. The bases quickly separated from the

potash solution and floated on its surface. The lye was then slowly run off by opening the bottom of the funnel, and when the whole of it was removed the escape of the bases was prevented by again closing the neck of the funnel. This operation was repeated till the whole of the ammonia was removed. A quantity of the bases remained dissolved in the alkaline lye, occasioning a loss, which however was unavoidable. The next step was to free the bases from the water they had absorbed, and which appeared to be nearly equal to that of their own bulk. The water was pretty readily removed by agitating the bases with bits of fused potash, so long as the alkali appeared to be in the least degree moistened. In order to ensure their being perfectly anhydrous, the bases were treated with successive quantities of fresh potash, and were kept in contact with the last portion for nearly a week. The clear liquid was then poured off from the potash into a small glass retort and cautiously rectified. The first two-thirds of the liquid which came over was a colourless transparent oil. The last portions, which distilled at a much higher temperature, had a slightly yellow colour, which increased in depth towards the close of the distillation. The colourless and the coloured portions were therefore collected separately. By repeated rectifications, however, the last portions of the bases were freed from the resinous matter they contained, and rendered as transparent and colourless as the first portion. As it was plain from the great variation in their boiling-points that the liquids were not homogeneous but consisted of a mixture of bases, many attempts were made to obtain them in a separate state by means of fractionated distillation. A thermometer was therefore inserted into the mixture of the bases by means of a perforated cork passed through the tubes of the retort. The mixture began to boil at 108° C., when a very small portion of a limpid colourless oil, which was collected separately, distilled over. The thermometer rapidly rose to 120° C., and from that to 130°, at both of which points small portions of oil were also collected. The boiling-point remained stationary for a considerable time between 150° and 155° C., when a considerable quantity of the oil distilled over, and a second large quantity also came over between 160° and 165° C. The boiling-points of the last portions of the bases ranged between 165° C. and 220° C. The products of these different distillations were again repeatedly rectified, and by this means bases were obtained corresponding more closely with those points at which the thermometer remained longest during the first distillation. Though these various bases differed, as we have just seen, so considerably in their boiling-points, they still exhibited great similarity of character. Thus they formed transparent colourless oils which refracted the light very strongly. They were all lighter than water, and possessed the peculiar, pungent, slightly aromatic smell, so characteristic of this class of compounds. When brought in contact with the hands or with clothes, their odour was very persistent. The smell of the more volatile bases was, as might have been expected, the most pungent. Their taste was hot, and when diluted not disagreeable, reminding one of oil of peppermint. The bases which distilled over at low temperatures were tolerably soluble in water,

at any rate more soluble than those whose boiling-points were high. They all dissolved in every proportion in alcohol and in ether. The bases exhibited strong alkaline reactions with turmeric paper, and restored the blue colour of litmus. They caused abundant fumes when a rod moistened with muriatic acid was held over them, and they neutralized acids perfectly, forming in general crystallizable salt. They formed double salts with the bichlorides of gold, platinum and mercury. These compounds were soluble in water to nearly the same extent as the corresponding ammoniacal salts. The platinum salts crystallized in four-sided prisms arranged in stars. The salts, which the bases with high boiling-points formed, were however often contaminated with a brownish resin, and crystallized but imperfectly. This was the case also with the gold salts. The bases also precipitated the persalts of iron and those of copper just as ammonia does, forming like it a fine blue colour when the bases were in excess. Though kept for a considerable time in loosely-stoppered bottles, which were not unfrequently opened, they remained transparent and colourless; but if exposed to a strong light, especially those of them which had the highest boiling-points, they gradually became of a deep yellow colour. These bases were pretty readily oxidizable. When treated with nitric acid, they were rapidly changed into yellowish resins, but no charbazotic acid was produced. When brought in contact with hypochlorite of lime, they were also changed into brownish resins, but not a trace of aniline could be found, though it was carefully sought for. When the bases were boiled for a few minutes in a retort, they gradually became coloured, though the liquid which distilled over was as colourless as at first. At the close of the distillation a small quantity of resinous matter remained in the retort. I shall now subjoin some very imperfect analytical details, in order to give in the meantime some idea of the nature of these bases. I regret that the difficulty I have hitherto experienced in procuring them in large quantaties has prevented me from submitting them to the thorough examination they deserve, and which I hope ere long to accomplish. It is not that beans and other seeds, as we shall presently see, yield smaller quantities of bases than bones and other animal substances; on the contrary, their product in bases is equal to that obtained from the distillation of bones, and, as might have been expected, much greater than that from coal. The difficulty wholly arises from this circumstance, that as both bones and coal are regularly distilled on the largest scale for commercial purposes, the crude oils of both bones and coal may be easily procured in any quantity, and from these their respective series of bases may be readily prepared. In regard to the bases from beans and similar seeds, however, the case is very different, the scientific chemist requiring to distil these substances on purpose, an operation which cannot be conveniently conducted in a laboratory, as the necessary apparatus is so large as to be almost upon a manufacturing scale.

I. 0·298 grm. of the base, boiling between 150° and 155° C., when analysed gave 0·815 carbonic acid and 0·222 water.

II. 0·270 grm. gave 0·7405 Co^2 and 0·189 water.

			I.	II.
10 C	750·0	74·98	74·60	74·78
6 H	75·0	7·49	8·18	7·77
1 N	175·2	17·53		
	1000·0	100·00		

When the anhydrous base combined with muriatic acid much heat was evolved. The muriate was very soluble in water, but when sufficiently concentrated it crystallized in slender prisms. With sulphuric and nitric acids the base also formed similar compounds. The platinum double salt was readily procured by adding bichloride of platinum to a pretty concentrated solution of the base in muriatic acid. This salt crystallized in four-sided prisms, arranged in stars of a deep yellow colour. It was rather less soluble in water than the corresponding ammoniacal compound. It was purified by a second crystallization out of water, which freed it from a little resinous matter it was apt to contain at the first. The formula of this salt was $C_{10} H_6 N$, HCl, $PtCl_2$, and the calculated quantity of platinum 34·50 per cent.

I. 0·7314 grm. salt, dried *in vacuo*, gave 0·254 Pl=34·72 per cent.

II. 0·3150 grm. salt gave 0·109 Pl=34·60 per cent.

When chloride of gold was added to a solution of this base in muriatic acid, a double salt was immediately formed. It crystallized very readily in pale yellow needles, which were very soluble in hot water, and were again deposited on the cooling of the liquid.

It is evident that this base, the probable formula of which is $C_{10} H_6 N$, approaches very closely in its composition to nicotine, and in its characters to picoline, the base discovered by Dr. Anderson in coal-tar. The formula of nicotine is $C_{10} H_7 N$. The boiling-point of the new base is higher than that of picoline, and its solubility in water is much less. Dr. Anderson says that picoline is soluble in water in every proportion, while this base requires at least six or seven times its bulk of water to dissolve it. The new base was lighter than water. Its smell was peculiar and slightly aromatic. Its taste was hot, reminding one of peppermint. It dissolved in every proportion, both in alcohol and in ether. It remained colourless, though kept in an imperfectly stoppered bottle, if not exposed to a strong light. It caught fire readily, and burnt with a bright smoky flame.

In order to obtain an approximative idea of the per-centage composition of the other bases with which this was accompanied, three of them were subjected to analysis.

I. 0·2632 grm. of the base, or not improbably mixture of bases, boiling between 160° and 165° C., gave 0·715 carbonic acid and 0·191 water.

II. 0·239 grm. of the liquid, boiling between 165° and 170° C., gave 0·661 carbonic acid and 0·1835 water.

III. 0·197 grm., boiling between 200° and 210° C., gave 0·547 Co^2 and 0·155 water.

	I.	II.	III.
C	74·08	75·42	75·63
H	8·06	8·52	8·73

It is rather singular that the amount of carbon and hydrogen does not vary more, while the boiling-points of these bases, or not improbably mixture of bases, are so exceedingly different. They all form double salts with chlorides of gold and platinum. Those with the highest boiling-points do not crystallize so readily as the less volatile bases, and are apt to be contaminated with resinous matter. As the height of their boiling-points rises, the solubility of the bases in water diminishes. They all appear to possess equally strong basic properties. Their detailed examination must however be reserved for a future communication.

As the *Phaseolis communis* was selected as the representative of that numerous tribe of plants, the Leguminosæ, of which the various kinds of beans, peas, lentils, &c. are the most familiar examples, the next substance subjected to distillation was oil-cake, or the dried seeds of *Linum usitatissimum*, from which the fat oil had been expressed. Oil-cake was selected as the type of the numerous class of plants in which the starch of the Gramineæ is replaced by oil. Of these, the poppy, rape, mustard, &c. are the best known. They are all very rich in vegetable albumen. The oil-cake was broken into moderate-sized pieces and distilled in the same cylinders as were employed for the beans. The quantity on which I operated was about two hundred weight. It yielded, as might have been expected, a smaller amount of liquid products than the beans. Their odour was peculiarly offensive. They consisted of acetone, acetic acid, a great deal of tar and empyreumatic oils. The quantity of ammonia was also exceedingly great. I was however disappointed to find that the organic bases were much less than in the case of the beans, amounting to not more than a third of what they yielded. The only way in which I can account for this different result, is from the greatly higher temperature at which the oil-cake was distilled, the heat not being mitigated, as in the case of the beans, by the presence of much moisture. Now, as all these volatile alkaloids are when highly heated resolved into ammonia, I think there is every reason to conclude, that in this, as in many other instances, a large portion of the bases which would have been generated at a lower temperature, were either not formed at all, or were destroyed immediately after their formation. The large amount of ammonia and the deficiency of the other bases is thus very naturally accounted for. The bases from oil-cake were separated and purified by similar methods to those employed for the preceding bases. They also formed a different series from either the coal or the bone bases, as they contained neither aniline nor quinoline. Their odour also differed considerably from that of the bases from beans, which however they closely resembled in other respects; their basic properties were equally decided, and they also formed similar salts. It appears probable enough therefore that some of the bases in both series are identical. But on this subject I expect to be able to speak more decidedly in a future paper.

Wheat.

A considerable quantity of the flour of *Triticum hybernum*, or common wheat, was also destructively distilled. Wheat was selected as a type of the Gramineæ, a most important order of plants, of which barley, oats, maise, &c. are those with which we are most familiar.

The liquid which the wheat-flour yielded, unlike that of the two preceding substances, was strongly acid from the large quantity of acetic acid it contained, derived from the starchy matters of the grain. The amount of acetone and wood-spirit was also very considerable. The empyreumatic products had a much less offensive odour than those from either oil-cake or from beans. The amount of ammonia was by no means inconsiderable, but the quantity of organic bases was less than I expected. They amounted however to pretty nearly the same quantity as those yielded by oil-cake. They did not contain either aniline or quinoline, and closely resembled the two preceding series in their general characters. They seemed however to be more volatile, distilling over at a lower temperature. At present I shall confine myself to the statement, that wheat, and most probably the other Gramineæ when distinctly distilled, also yield organic bases. As the starch in wheat, the quantity of which is so considerable, only forms acetic acid and other non-nitrogenated products, I intend in repeating this experiment to employ the gluten from the starch-makers, which contains almost the whole of the nitrogen in the wheat, and being a refuse product can be had for a trifle.

Peat.

A quantity of peat from the moors in the neighbourhood of Glasgow was also destructively distilled. I selected for this purpose the densest peat I could find. It had a deep black colour, and was very free from earthy matters. The products of its distillation were very nearly neutral to test-paper, owing to the formation of a considerable amount of acetic acid. Acetone and wood-spirit were also present in considerable quantity. The crude liquor was saturated with muriatic acid and gently boiled for some time to drive off the acetone, wood-spirit, &c., by which much of the tarry matter was held in solution. On the cooling of the liquid, the tar readily solidified and formed a soft crust on the surface, which was easily removed. The clear liquid was then supersaturated with carbonate of soda and distilled. The ammoniacal liquor which passed into the receiver contained a considerable amount of bases, which floated in it as a light oil. These were freed from ammonia and purified by the same means as in the preceding instances. The bases from peat bore a much larger proportion to the amount of ammonia than was the case with oil-cake. I ascribe this result chiefly to the porous nature of peat which conducts heat but slowly, and also to the greater degree of moisture contained in it. The bases therefore being distilled at a much lower temperature, a smaller amount of them was resolved into ammonia than in the instance of oil-cake. I expected to have found

aniline among the bases, but they appeared to contain neither it nor quinoline. They resembled the preceding series pretty closely therefore, but whether they will prove identical with them or not I am at present unable to say.

Distillation of Wood.

Through the kindness of Mr. TURNBULL, an extensive manufacturer of pyroligneous acid in this city, I was enabled to examine considerable quantities of the crude acid liquor obtained from the destructive distillation of beech, oak, ash and other hard woods. The stems and the larger branches of these trees are alone employed for this purpose. I was astonished to find that these liquors contained scarcely a trace of ammonia or any other organic bases. The woody portions therefore of the stems and trunks of trees appear to be almost entirely devoid of nitrogenous matter, in which respect they exhibit a remarkable contrast to peat.

This circumstance appears to me as perhaps calculated to throw some light upon a question of great interest to geologists, viz. the origin of the coal-beds. Whether therefore have the coal-beds been formed by the submersion of whole forrests and the floating of uprooted timber into estuaries and lakes, or whether are they due to the submersion of beds of peat? Now irrespective of all other considerations which might be urged in favour of the latter opinion, I would remark that the amount of nitrogen in coal, and consequently the quantity of ammonia and other bases which it yields when destructively distilled, are very considerable, constituting in fact an extensive branch of chemical manufacture. Wood, however, as we have just seen, appears to be quite incapable of furnishing the amount of nitrogen which we find existing in coal. Peat, on the other hand, from the quantity of ammonia and other bases which it yields when destructively distilled, is capable of furnishing more than the required amount of ammonia. This circumstance appears therefore highly confirmatory of the opinion, that the true source of coal is only to be sought for in peat.

As was already observed, I expected to have been able to procure from peat, in addition to ammonia, aniline, quinoline, picoline and the other coal bases. I did not find these however, but merely an analogous series of bases. I can only account for this result on the assumption that the different genera of plants, when destructively distilled, yield different series of organic bases. This we already know to be the case in several instances; for when indigo or any of the indigoferæ are destructively distilled, they yield ammonia and aniline; tobacco leaves, when similarly treated, yield ammonia and nicotine; the different species of the Peruvian bark, quinoline, and beans, wheat, oil-cake, &c., as we have already seen, do not yield aniline and quinoline, but are analogous series of bases. I am induced to believe therefore that the reason why modern peat does not yield the identical bases found in coal is, because the peat beds of primitive times, which in the course of ages have been converted into coal, were formed from the decaying remains of quite different plants than the various species of Erica and those other vegetables which constitute the peat

mosses of the present day. Had the plants in both cases been the same, I see no reason for doubting that when distilled they would have yielded identical bases.

Formation of Organic Bases from the nitrogenous Principles of Vegetables and Animals otherwise than by destructive Distillation.

1. *By treating them with alkaline lyes.*—From the facts which have been previously stated, I think we are warranted to conclude, that when ammonia is produced in large quantities by the destructive distillation of either vegetable or animal substances, it is always accompanied by the formation of organic bases. Now as ammonia is known to be procurable from these substances by several other methods, it seemed by no means improbable that on these occasions organic bases would also be produced. It has long been known that ammonia is largely generated when the nitrogenous portions of either plants or animals are boiled with strong alkaline lyes. A quantity of beans was therefore introduced into the body of a large still, and was boiled with a strong solution of caustic soda. The beans were speedily disintegrated, being converted into a slimy, dark-coloured pulp. The greatest difficulty attending the operation was caused by the frothing up of the pasty mixture, which, unless the still was very capacious and the fire kept moderate, was very apt to boil over and choke up the worm of the distilling apparatus. By cautiously rectifying the product of the distillation, a clear, strongly alkaline liquid was procured. It contained a large amount of ammonia, a little of a very agreeably smelling aromatic oil, and a considerable quantity of organic bases. The liquid was neutralized with muriatic acid, and the aromatic oil separated by means of a moist filter. On supersaturating with caustic soda and redistilling it, a strongly ammoniacal liquid passed into the receiver. It contained a considerable quantity of oily bases, partly in solution and partly floating on the liquid. These bases closely resemble those obtained by destructively distilling the beans, but whether they will prove identical with them or not I am at present unable to say.

Oil-cake was also distilled with a strong soda lye. It also yielded ammonia and similar organic bases. I should therefore expect that the same results will be obtained with the corresponding nitrogenous portions of most other plants.

Part II.

Bases from Flesh by the Action of Caustic Lyes.

An ox-liver was cut into moderate sized pieces, and introduced into the body of a capacious still containing a quantity of tolerably strong caustic soda. The liver, speedily dissolved, formed a brownish and very liquid jelly, which frothed up exceedingly. A strongly ammoniacal liquid distilled over accompanied by an aromatic oil, very similar to that obtained from the beans. The ammoniacal liquid was neutralized with muriatic acid and concentrated. During this operation the aromatic

oil was converted into a brownish resin. The concentrated liquid was then supersaturated with carbonate of soda and redistilled. The ammoniacal solution which came over contained a considerable quantity of oily bases. I am at present unable to state what these bases are, but hope to do so in the course of a few weeks. One advantage in operating with caustic lyes is, that the bases are immediately obtained quite free from empyreumatic oils or resins.

2. *Formation of Bases by means of Sulphuric Acid.*—A quantity of beans was also digested with sulphuric acid, diluted with three or four times its bulk of water. The beans, as in the previous instance, were speedily disintegrated. Care was taken to prevent the action proceeding so far as to decompose the sulphuric acid and to generate sulphurous acid. The strongly acid liquid, after being filtered, was supersaturated with carbonate of soda and distilled. The ammoniacal liquid which passed into the receiver was, on examination, found also to contain organic bases. I think it may be inferred, therefore, that when other vegetable and animal substances are similarly treated they will also yield analogous results.

3. *Bases by Putrefaction.*—Putrefaction is the only other method I at present recollect by which ammonia is procurable, in quantity, from animal and vegetable substances. I have not at the moment an opportunity of ascertaining whether in these cases also the ammonia is accompanied with the formation of organic bases, though I feel strongly inclined to believe that it is. The peculiarly disagreeable odour of the ammoniacal liquors, derived from putrid substances, appears to indicate the presence of such bases. And I should not be at all surprised, if, from the very gentle nature of the process, putrefaction should prove to be the most advantageous method of preparing the volatile alkaloids on a large scale.

Guano.

Since the above was written, I distilled an aqueous solution of a quantity of Peruvian guano with an excess of quick-lime. The guano had a pale yellow colour, was very dry, and emitted a comparatively feeble odour. The strong ammoniacal liquid which distilled over was neutralized with muriatic acid, and concentrated to about a third of its bulk. It was then supersaturated with carbonate of soda and redistilled. The liquid which passed into the receiver contained a small, but very appreciable quantity of a basic oil, similar to that obtained from the preceding substances. Muriatic acid dissolved it very readily, forming a transparent solution, from which it was precipitated by alkalies. It was considerably more soluble in water than any of the bases previously described. Its amount was less than I expected, though guano cannot be regarded as a favourable example of the usual effects of putrefaction on a complex nitrogenous substance, as the chief portion of the nitrogen contained in it existed from the first in the state of ammoniacal salts. Guano, however, in addition to ammonia, also contains a quantity of volatile organic bases.

From the facts which have been now stated, I think it may be pretty safely

assumed, that "*whenever ammonia is generated in large quantity from complex, either animal or vegetable substances, it is always accompanied by the formation of a larger or smaller amount of volatile organic bases.*" If therefore researches similar to the present are actively prosecuted, and if the seeds and leaves of the various genera of plants especially are subjected to these or similar processes, it seems not unreasonable to expect that the number of the volatile organic alkaloids will ere long be considerably increased.

Another inference which we think may be fairly deduced from these experiments is, that the nitrogenous principles of plants, viz. vegetable albumen, caseine, fibrine, &c., though very analogous, are not identical with the corresponding principles of the animal kingdom, otherwise the products of their decomposition would have been the same. The same series of bases would therefore have been obtained from both beans and bones, and so also from the other animal and vegetable substances. This, as we have seen, however, is not the case; I should therefore be disposed to conclude that animal and vegetable fibrine, caseine, &c., though very analogous, are not identical substances, as has hitherto been supposed by some eminent chemists.

In conducting the destructive distillation of animal and vegetable substances, the chief point to be attended to is to operate at as low a temperature as possible, for I have not unfrequently found that when the heat had been inadvertently raised too high the organic bases were almost entirely destroyed, and ammonia was consequently almost the only alkaline product. I strongly suspect, therefore, that in many cases a considerable portion of the ammonia obtained from the distillation of animal and vegetable substances is really derived from the destruction of organic bases. This will appear still more probable when we consider that the organic bases are more complex in their structure than ammonia, and that if we pass even the most stable of them once or twice through a tube filled with red-hot charcoal, they are almost entirely resolved into that alkali. And even when organic bases are strongly heated in contact with potash or soda, or when their aqueous solutions are simply boiled for any length of time, they always undergo partial decomposition, ammonia being an invariable product.

I must again apologize for the imperfect state of this paper. It is however merely the first of a series, and will, I trust, be regarded as only preliminary to more mature investigations.

Glasgow, 11*th June*, 1849.

Addendum to the paper on the Nitrogenous principles of Vegetables as the sources of artificial Alkaloids.

Since the preceding paper was written several additional experiments have been made, some of the results of which I now beg leave to subjoin.

Bases by putrefaction.

A quantity of horse-flesh which had been cut into small pieces and the juice extracted by long-continued boiling, was moistened with water and was placed in a warm situation for nearly a month. It became very putrid and was full of maggots. It was then supersaturated with muriatic acid, and repeatedly agitated with water so long as anything was dissolved. The acid liquor was superfluous, concentrated to a moderate bulk, and filtered to remove the flocculent and albuminous matters collected in it. The clear liquid was next supersaturated with carbonate of soda and subjected to distillation. A highly alkaline liquor came over, consisting chiefly of carbonate of ammonia, but mixed with small quantities of organic bases. By repeated rectifications with caustic soda, a quantity of a light oily fluid consisting of one or more bases was separated. It had a pleasant aromatic odour, and was exceedingly soluble in water, from which however it separated, when sufficiently concentrated, as a transparent colourless oil, which was strongly alkaline, saturating acids and forming salts similar to those of the preceding bases. I was surprised however to find that it did not contain any aniline. The quantity of organic bases obtained by this experiment, though very appreciable in amount, was not nearly so great as I had anticipated; as, instead of yielding more than was obtained by destructive distillation, it gave a great deal less. Had however the superfluous putrefaction been carried far enough, and the whole of the flesh been decomposed, it is not improbable that as large or even a greater amount of bases would have been obtained as by destructive distillation; but a great deal of time would have been required to have effected the complete decomposition of the flesh by simple putrefaction. The present experiment however sufficiently proves that putrefaction forms no exception to the law I have ventured to lay down in a preceding part of this paper, viz. "that whenever ammonia is generated in quantity from a complex organic substance, it is always accompanied by the production of a larger or smaller amount of organic bases." It is also remarkable that the putrefaction of flesh in this instance yielded no aniline, which is a constant and considerable product when either flesh or bones are destructively distilled. The nature of the organic bases obtainable from the decomposition of nitrogenous substances appears to be dependent therefore on the processes to which they are subjected.

Bases from Lycopodium.

A quantity of lycopodium (pollen) was boiled with some strong soda-lye, and then evaporated to dryness. It was next destructively distilled in an iron retort, and the

products collected in the way already so frequently described. Besides much ammonia they contained a considerable quantity of a basic oil but slightly soluble in water, of a very peculiar and penetrating odour resembling that of the borage plant. It neutralized acids perfectly, and was evidently quite distinct from any of the bases previously met with. A quantity of lycopodium destructively distilled *per se* also yielded this base, but towards the close of the distillation it was mixed with other bases resembling those previously described. Lycopodium therefore affords us another proof that different tribes of vegetables, when destructively distilled, furnish a diversity of volatile organic bases.

Bases from the Common Fern (Pteris aquilina).

A quantity of the stems and leaves of the fern *Pteris aquilina* were also destructively distilled. They yielded a very alkaline liquid, containing much ammonia and a considerable quantity of oily bases similar in character to those obtained from beans, oil-cake, &c.; but I am at present unable to determine their nature individually.

III. *On the Mechanical Equivalent of Heat.* By James Prescott Joule, *F.C.S., Sec. Lit. and Phil. Society, Manchester, Cor. Mem. R.A., Turin, &c. Communicated by* Michael Faraday, *D.C.L., F.R.S., Foreign Associate of the Academy of Sciences, Paris, &c. &c. &c.*

Received June 6,—Read June 21, 1849.

"Heat is a very brisk agitation of the insensible parts of the object, which produces in us that sensation from whence we denominate the object hot; so what in our sensation is *heat*, in the object is nothing but *motion*."—Locke.

"The *force* of a moving body is proportional to the square of its velocity, or to the height to which it would rise against gravity."—Leibnitz.

In accordance with the pledge I gave the Royal Society some years ago, I have now the honour to present it with the results of the experiments I have made in order to determine the mechanical equivalent of heat with exactness. I will commence with a slight sketch of the progress of the mechanical doctrine, endeavouring to confine myself, for the sake of conciseness, to the notice of such researches as are immediately connected with the subject. I shall not therefore be able to review the valuable labours of Mr. Forbes and other illustrious men, whose researches on radiant heat and other subjects do not come exactly within the scope of the present memoir.

For a long time it had been a favourite hypothesis that heat consists of "a force or power belonging to bodies*," but it was reserved for Count Rumford to make the first experiments decidedly in favour of that view. That justly celebrated natural philosopher demonstrated by his ingenious experiments that the very great quantity of heat excited by the boring of cannon could not be ascribed to a change taking place in the calorific capacity of the metal; and he therefore concluded that the motion of the borer was communicated to the particles of metal, thus producing the phenomena of heat:—"It appears to me," he remarks, "extremely difficult, if not quite impossible, to form any distinct idea of anything, capable of being excited and communicated, in the manner the heat was excited and communicated in these experiments, except it be motion†."

One of the most important parts of Count Rumford's paper, though one to which

* Crawford on Animal Heat, p. 15.

† "An Inquiry concerning the Source of the Heat which is excited by Friction." Phil. Trans. Abridged, vol. xviii. p. 286.

little attention has hitherto been paid, is that in which he makes an estimate of the quantity of mechanical force required to produce a certain amount of heat. Referring to his third experiment, he remarks that the "total quantity of ice-cold water which, with the heat actually generated by friction, and accumulated in $2^h\ 30^m$, might have been heated 180°, or made to boil,=26·58 lbs." * In the next page he states that "the machinery used in the experiment could easily be carried round by the force of one horse (though, to render the work lighter, two horses were actually employed in doing it)." Now the power of a horse is estimated by WATT at 33,000 foot-pounds per minute, and therefore if continued for two hours and a half will amount to 4,950,000 foot-pounds, which, according to Count RUMFORD's experiment, will be equivalent to 26·58 lbs. of water raised 180°. Hence the heat required to raise a lb. of water 1° will be equivalent to the force represented by 1034 foot-pounds. This result is not very widely different from that which I have deduced from my own experiments related in this paper, viz. 772 foot-pounds; and it must be observed that the excess of Count RUMFORD's equivalent is just such as might have been anticipated from the circumstance, which he himself mentions, that "no estimate was made of the heat accumulated in the wooden box, nor of that dispersed during the experiment."

About the end of the last century Sir HUMPHRY DAVY communicated a paper to Dr. BEDDOES' West Country Contributions, entitled, "Researches on Heat, Light and Respiration," in which he gave ample confirmation to the views of Count RUMFORD. By rubbing two pieces of ice against one another in the vacuum of an air-pump, part of them was melted, although the temperature of the receiver was kept below the freezing-point. This experiment was the more decisively in favour of the doctrine of the immateriality of heat, inasmuch as the capacity of ice for heat is much less than that of water. It was therefore with good reason that DAVY drew the inference that "the immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion†."

The researches of DULONG on the specific heat of elastic fluids were rewarded by the discovery of the remarkable fact that "equal volumes of all the elastic fluids, taken at the same temperature, and under the same pressure, being compressed or dilated suddenly to the same fraction of their volume, disengage or absorb the same *absolute quantity of heat*‡." This law is of the utmost importance in the development of the theory of heat, inasmuch as it proves that the calorific effect is, under certain conditions, proportional to the force expended.

In 1834 Dr. FARADAY demonstrated the "Identity of the Chemical and Electrical Forces." This law, along with others subsequently discovered by that great man, showing the relations which subsist between magnetism, electricity and light, have

* "An Inquiry concerning the Source of the Heat which is excited by Friction." Phil. Trans. Abridged, vol. xviii. p. 283.

† Elements of Chemical Philosophy, p. 94.

‡ Mémoires de l'Académie des Sciences, t. x. p. 188.

enabled him to advance the idea that the so-called imponderable bodies are merely the exponents of different forms of Force. Mr. Grove and M. Mayer have also given their powerful advocacy to similar views.

My own experiments in reference to the subject were commenced in 1840, in which year I communicated to the Royal Society my discovery of the law of the heat evolved by voltaic electricity, a law from which the immediate deductions were drawn,—1st, that the heat evolved by any voltaic pair is proportional, *cæteris paribus*, to its intensity or electromotive force*; and 2nd, that the heat evolved by the combustion of a body is proportional to the intensity of its affinity for oxygen†. I thus succeeded in establishing relations between heat and chemical affinity. In 1843 I showed that the heat evolved by magneto-electricity is proportional to the force absorbed; and that the force of the electro-magnetic engine is derived from the force of chemical affinity in the battery, a force which otherwise would be evolved in the form of heat: from these facts I considered myself justified in announcing "that the quantity of heat capable of increasing the temperature of a lb. of water by one degree of Fahrenheit's scale, is equal to, and may be converted into, a mechanical force capable of raising 838 lbs. to the perpendicular height of one foot‡."

In a subsequent paper, read before the Royal Society in 1844, I endeavoured to show that the heat absorbed and evolved by the rarefaction and condensation of air is proportional to the force evolved and absorbed in those operations§. The quantitative relation between force and heat deduced from these experiments, is almost identical with that derived from the electro-magnetic experiments just referred to, and is confirmed by the experiments of M. Seguin on the dilatation of steam‖.

From the explanation given by Count Rumford of the heat arising from the friction of solids, one might have anticipated, as a matter of course, that the evolution of heat would also be detected in the friction of liquid and gaseous bodies. Moreover there were many facts, such as, for instance, the warmth of the sea after a few days of stormy weather, which had long been commonly attributed to fluid friction. Nevertheless the scientific world, preoccupied with the hypothesis that heat is a substance, and following the deductions drawn by Pictet from experiments not sufficiently delicate, have almost unanimously denied the possibility of generating heat in that way. The first mention, so far as I am aware, of experiments in which the evolution of heat from fluid friction is asserted, was in 1842 by M. Mayer¶, who states that he has raised the temperature of water from 12° C. to 13° C., by agitating it, without however indicating the quantity of force employed, or the precautions taken to secure a correct result. In 1843 I announced the fact that "heat is evolved by the passage of water through narrow tubes**," and that each degree of heat per lb. of water required for its evolution in this way a mechanical force represented by

* Phil. Mag. vol. xix. p. 275. † Ibid. vol. xx. p. 111. ‡ Ibid. vol. xxiii. p. 441.
§ Ibid. vol. xxvi. pp. 375. 379. ‖ Comptes Rendus, t. 25, p. 421.
¶ Annalen of Wœhler and Liebig, May 1842. ** Phil. Mag. vol. xxiii. p. 442.

770 foot-pounds. Subsequently, in 1845* and 1847†, I employed a paddle-wheel to produce the fluid friction, and obtained the equivalents 781·5, 782·1 and 787·6, respectively, from the agitation of water, sperm-oil and mercury. Results so closely coinciding with one another, and with those previously derived from experiments with elastic fluids and the electro-magnetic machine, left no doubt on my mind as to the existence of an equivalent relation between force and heat; but still it appeared of the highest importance to obtain that relation with still greater accuracy. This I have attempted in the present paper.

Description of Apparatus.—The thermometers employed had their tubes calibrated and graduated according to the method first indicated by M. Regnault. Two of them, which I shall designate by A and B, were constructed by Mr. Dancer of Manchester; the third, designated by C, was made by M. Fastré of Paris. The graduation of these instruments was so correct, that when compared together their indications coincided to about $\frac{1}{100}$th of a degree Fahr. I also possessed another exact instrument made by Mr. Dancer, the scale of which embraced both the freezing and boiling-points. The latter point in this standard thermometer was obtained, in the usual manner, by immersing the bulb and stem in the steam arising from a considerable quantity of pure water in rapid ebullition. During the trial the barometer stood at 29·94 inches, and the temperature of the air was 50°; so that the observed point required very little correction to reduce it to 0·760 metre and 0° C., the pressure used in France, and I believe the Continent generally, for determining the boiling-point, and which has been employed by me on account of the number of accurate thermometrical researches which have been constructed on that basis‡. The values of the scales of thermometers A and B were ascertained by plunging them along with the standard in large volumes of water kept constantly at various temperatures. The value of the scale of thermometer C was determined by comparison with A. It was thus found that the number of divisions corresponding to 1° Fahr. in the thermometers A, B and C, were 12·951, 9·829 and 11·647, respectively. And since constant practice had enabled me to read off with the naked eye to $\frac{1}{10}$th of a division, it followed that $\frac{1}{100}$th of a degree Fahr. was an appreciable temperature.

Plate VII. fig. 1 represents a vertical, and fig. 2 a horizontal plan of the apparatus employed for producing the friction of water, consisting of a brass paddle-wheel furnished with eight sets of revolving arms, *a*, *a*, &c., working between four sets of stationary vanes,

* Phil. Mag., vol. xxvii. p. 205. † Ibid. vol. xxxi. p. 173, and Comptes Rendus, tome xxv. p. 309.

‡ A barometrical pressure of 30 inches of mercury at 60° is very generally employed in this country, and fortunately agrees almost exactly with the continental standard. In the "Report of the Committee appointed by the Royal Society to consider the best method of adjusting the Fixed Points of Thermometers," Philosophical Transactions, Abridged, xiv. p. 258, the barometrical pressure 29·8 is recommended, but the temperature is not named,—a remarkable omission in a work so exact in other respects.

b, *b*, &c., affixed to a framework also in sheet brass. The brass axis of the paddle-wheel worked freely, but without shaking, on its bearings at *c*, *c*, and at *d* was divided into two parts by a piece of boxwood intervening, so as to prevent the conduction of heat in that direction.

Fig. 3 represents the copper vessel into which the revolving apparatus was firmly fitted: it had a copper lid, the flange of which, furnished with a very thin washer of leather saturated with white-lead, could be screwed perfectly water-tight to the flange of the copper vessel. In the lid there were two necks, *a*, *b*, the former for the axis to revolve in without touching, the latter for the insertion of the thermometer.

Besides the above I had a similar apparatus for experiments on the friction of mercury, which is represented by figs. 4, 5 and 6. It differed from the apparatus already described in its size; number of vanes, of which six were rotary and eight sets stationary; and material, which was wrought iron in the paddle-wheel, and cast iron in the vessel and lid.

Being anxious to extend my experiments to the friction of solids, I also procured the apparatus represented by fig. 7, in which *a a* is the axis revolving along with the beveled cast-iron wheel *b*, the rim of which was turned true. By means of the lever *c*, which had a ring in its centre for the axis to pass through, and two short arms *d*, the bevel turned cast-iron wheel *e* could be pressed against the revolving wheel; the degree of force applied being regulated by hand by means of the wooden lever *f* attached to the perpendicular iron rod *g*. Fig. 8 represents the apparatus in its cast-iron vessel.

Fig. 9 is a perspective view of the machinery employed to set the frictional apparatus just described in motion. *a a* are wooden pulleys, 1 foot in diameter and 2 inches thick, having wooden rollers *b b*, *b b*, 2 inches in diameter, and steel axles *c c*, *c c*, one quarter of an inch in diameter. The pulleys were turned perfectly true and equal to one another. Their axles were supported by brass friction wheels *dddd*, *dddd*, the steel axles of which worked in holes drilled into brass plates attached to a very strong wooden framework firmly fixed into the walls of the apartment*.

The leaden weights *e*, *e*, which in some of the ensuing experiments weighed about 29 lbs., and in others about 10 lbs. a piece, were suspended by string from the rollers *b b*, *b b*; and fine twine attached to the pulleys *a a*, connected them with the central roller *f*, which, by means of a pin, could with facility be attached to, or removed from, the axis of the frictional apparatus.

The wooden stool *g*, upon which the frictional apparatus stood, was perforated by a number of transverse slits, so cut out that only a very few points of wood came in contact with the metal, whilst the air had free access to almost every part of it. In this way the conduction of heat to the substance of the stool was avoided.

* This was a spacious cellar, which had the advantage of possessing an uniformity of temperature far superior to that of any other laboratory I could have used.

A large wooden screen (not represented in the figure) completely obviated the effects of radiant heat from the person of the experimenter.

The method of experimenting was simply as follows:—The temperature of the frictional apparatus having been ascertained and the weights wound up with the assistance of the stand *h*, the roller was refixed to the axis. The precise height of the weights above the ground having then been determined by means of the graduated slips of wood *k*, *k*, the roller was set at liberty and allowed to revolve until the weights reached the flagged floor of the laboratory, after accomplishing a fall of about 63 inches. The roller was then removed to the stand, the weights wound up again, and the friction renewed. After this had been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the laboratory was determined by observations made at the commencement, middle and termination of each experiment.

Previously to, or immediately after each of the experiments, I made trial of the effect of radiation and conduction of heat to or from the atmosphere, in depressing or raising the temperature of the frictional apparatus. In these trials, the position of the apparatus, the quantity of water contained by it, the time occupied, the method of observing the thermometers, the position of the experimenter, in short everything, with the exception of the apparatus being at rest, was the same as in the experiments in which the effect of friction was observed.

1*st Series of Experiments.*—Friction of Water. Weight of the leaden weights along with as much of the string in connexion with them as served to increase the pressure, 203066 grs. and 203086 grs. Velocity of the weights in descending, 2·42 inches per second. Time occupied by each experiment, 35 minutes. Thermometer employed for ascertaining the temperature of the water, A. Thermometer for registering the temperature of the air, B.

TABLE I.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
1 Friction	1256·96	57°·698	2°·252—	55°·118	55°·774	0°·656 gain
1 Radiation ...	0	57·868	2·040—	55·774	55·882	0·108 gain
2 Friction	1255·16	58·085	1·875—	55·882	56·539	0·657 gain
2 Radiation ...	0	58·370	1·789—	56·539	56·624	0·085 gain
3 Friction	1253·66	60·788	1·596—	58·870	59·515	0·645 gain
3 Radiation ...	0	60·926	1·373—	59·515	59·592	0·077 gain
4 Friction	1252·74	61·001	1·110—	59·592	60·191	0·599 gain
4 Radiation ...	0	60·890	0·684—	60·191	60·222	0·031 gain
1	2	3	4	5	6	7

TABLE I. (Continued.)

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
5 Friction.....	1251·81	60°·940	0°·431—	60°·222	60°·797	0°·575 gain
5 Radiation ...	0	61·035	0·237—	60·797	60·799	0·002 gain
6 Radiation ...	0	59·675	0·125+	59·805	59·795	0·010 loss
6 Friction ...	1254·71	59·919	0·157+	59·795	60·357	0·562 gain
7 Radiation ...	0	59·888	0·209—	59·677	59·681	0·004 gain
7 Friction.....	1254·02	60·076	0·111—	59·681	60·249	0·568 gain
8 Radiation ...	0	58·240	0·609+	58·871	58·828	0·043 loss
8 Friction.....	1251·22	58·237	0·842+	58·828	59·330	0·502 gain
9 Friction.....	1253·92	55·328	0·070+	55·118	55·678	0·560 gain
9 Radiation ...	0	55·528	0·148+	55·678	55·674	0·004 loss
10 Radiation ...	0	54·941	0·324—	54·614	54·620	0·006 gain
10 Friction.....	1257·96	54·985	0·085—	54·620	55·180	0·560 gain
11 Radiation ...	0	55·111	0·069+	55·180	55·180	0·000
11 Friction.....	1258·59	55·229	0·227+	55·180	55·733	0·553 gain
12 Friction.....	1258·71	55·433	0·238+	55·388	55·954	0·566 gain
12 Radiation ...	0	55·687	0·265+	55·954	55·950	0·004 loss
13 Friction.....	1257·91	55·677	0·542+	55·950	56·488	0·538 gain
13 Radiation ...	0	55·674	0·800+	56·488	56·461	0·027 loss
14 Radiation ...	0	55·379	0·583—	54·987	55·006	0·019 gain
14 Friction.....	1259·69	55·864	0·568—	55·006	55·587	0·581 gain
15 Radiation ...	0	56·047	0·448—	55·587	55·612	0·025 gain
15 Friction.....	1259·89	56·182	0·279—	55·612	56·195	0·583 gain
16 Friction.....	1259·64	55·368	0·099+	55·195	55·739	0·544 gain
16 Radiation ...	0	55·483	0·250+	55·739	55·728	0·011 loss
17 Friction.....	1259·64	55·498	0·499+	55·728	56·266	0·538 gain
17 Radiation ...	0	55·541	0·709+	56·266	56·235	0·031 loss
18 Radiation ...	0	56·769	1·512—	55·230	55·284	0·054 gain
18 Friction.....	1260·17	56·966	1·372—	55·284	55·905	0·621 gain
19 Radiation ...	0	60·058	1·763—	58·257	58·334	0·077 gain
19 Friction.....	1262·24	60·112	1·450—	58·334	58·990	0·656 gain
20 Radiation ...	0	60·567	1·542—	58·990	59·060	0·070 gain
20 Friction.....	1261·94	60·611	1·239—	59·060	59·685	0·625 gain
21 Friction.....	1264·07	58·654	0·321—	58·050	58·616	0·566 gain
21 Radiation ...	0	58·627	0·018—	58·616	58·603	0·013 loss
22 Friction.....	1262·97	58·631	0·243+	58·603	59·145	0·542 gain
22 Radiation ...	0	58·624	0·505+	59·145	59·114	0·031 loss
23 Friction.....	1264·72	59·689	1·100—	58·284	58·894	0·610 gain
23 Radiation ...	0	59·943	1·027—	58·894	58·938	0·044 gain
1	2	3	4	5	6	7

TABLE I. (Continued.)

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
24 Radiation ...	0	60°·157	1°·160 —	58°·977	59°·017	0°·040 gain
24 Friction	1263·94	59·811	0·505 —	59·017	59·595	0·578 gain
25 Radiation ...	0	59·654	0·061 —	59·595	59·591	0·004 loss
25 Friction	1263·49	59·675	0·185 +	59·591	60·129	0·538 gain
26 Radiation ...	0	59·156	0·609 —	58·541	58·554	0·013 gain
26 Friction	1263·49	59·333	0·488 —	58·554	59·137	0·583 gain
27 Friction	1263·99	59·536	0·198 —	59·054	59·623	0·569 gain
27 Radiation ...	0	59·726	0·101 —	59·623	59·627	0·004 gain
28 Friction	1263·99	59·750	0·155 +	59·627	60·183	0·556 gain
28 Radiation ...	0	59·475	0·102 +	59·585	59·569	0·016 loss
29 Friction	1263·31	58·695	0·182 —	58·230	58·796	0·566 gain
29 Radiation ...	0	58·906	0·108 —	58·796	58·801	0·005 gain
30 Radiation ...	0	59·770	1·286 —	58·454	58·515	0·061 gain
30 Friction	1263·99	60·048	1·223 —	58·515	59·135	0·620 gain
31 Friction	1263·49	59·343	0·022 +	59·091	59·639	0·548 gain
31 Radiation ...	0	59·435	0·198 +	59·639	59·627	0·012 loss
32 Radiation ...	0	59·374	0·357 —	59·015	59·020	0·005 gain
32 Friction	1263·49	59·407	0·105 —	59·020	59·585	0·565 gain
33 Radiation ...	0	59·069	0·201 —	58·867	58·870	0·003 gain
33 Friction	1263·49	59·234	0·081 —	58·870	59·436	0·566 gain
34 Friction	1262·99	56·328	0·331 +	56·387	56·932	0·545 gain
34 Radiation ...	0	56·643	0·287 +	56·932	56·929	0·003 loss
35 Friction	1262·99	56·790	0·413 +	56·929	57·477	0·548 gain
35 Radiation ...	0	56·772	0·687 +	57·477	57·442	0·035 loss
36 Radiation ...	0	55·839	0·304 —	55·527	55·543	0·016 gain
36 Friction	1262·99	56·114	0·281 —	55·543	56·124	0·581 gain
37 Radiation ...	0	56·257	0·127 —	56·124	56·137	0·013 gain
37 Friction	1262·99	56·399	0·024 +	56·137	56·709	0·572 gain
38 Radiation ...	0	55·826	0·065 —	55·759	55·764	0·005 gain
38 Friction	1262·99	55·951	0·093 +	55·764	56·325	0·561 gain
39 Radiation ...	0	56·101	0·220 +	56·325	56·317	0·008 loss
39 Friction	1262·99	56·182	0·409 +	56·317	56·865	0·548 gain
40 Friction	1262·99	56·108	0·100 +	55·929	56·488	0·559 gain
40 Radiation ...	0	56·454	0·036 +	56·488	56·492	0·004 gain
Mean Friction...	1260·248	.....	0·305075—	.....	.....	0·575250 gain
Mean Radiation.	0	.....	0·322950—	.....	.....	0·012975 gain
1	2	3	4	5	6	7

From the various experiments in the above Table in which the effect of radiation was observed, it may be readily gathered that the effect of the temperature of the surrounding air upon the apparatus was, for each degree of difference between the mean temperature of the air and that of the apparatus, 0°·04654. Therefore, since the excess of the temperature of the atmosphere over that of the apparatus was 0°·32295 in the mean of the radiation experiments, but only 0°·305075 in the mean of the friction experiments, it follows that 0°·000832 must be added to the difference between 0°·57525 and 0°·012975, and the result, 0°·563107, will be the proximate heating effect of the friction. But to this quantity a small correction must be applied on account of the mean of the temperatures of the apparatus at the commencement and termination of each friction experiment having been taken for the true mean temperature, which was not strictly the case, owing to the somewhat less rapid increase of temperature towards the termination of the experiment when the water had become warmer. The mean temperature of the apparatus in the friction experiments ought therefore to be estimated 0°·002184 higher, which will diminish the heating effect of the atmosphere by 0°·000102. This, added to 0°·563107, gives 0°·563209 as the true mean increase of temperature due to the friction of water*.

In order to ascertain the absolute quantity of heat evolved, it was necessary to find the capacity for heat of the copper vessel and brass paddle-wheel. That of the former was easily deduced from the specific heat of copper according to M. Regnault. Thus, capacity of 25541 grs.† of copper × 0·09515 = capacity of 2430·2 grs. of water. A series of seven very careful experiments with the brass paddle-wheel gave me 1783 grs. of water as its capacity, after making all the requisite corrections for the heat occasioned by the contact of the water with the surface of the metal, &c. But on account of the magnitude of these corrections, amounting to one-thirtieth of the whole capacity, I prefer to avail myself of M. Regnault's law, viz. *that the capacity in metallic alloys is equal to the sum of the capacities of their constituent metals*‡. Analysis of a part of the wheel proved it to consist of a very pure brass containing 3933 grs. of zinc. to 14968 grs. of copper. Hence

Cap. 14968 grs. copper × 0·09515 = cap. 1424·2 grs. water.
Cap. 3933 grs. zinc × 0·09555 = cap. 375·8 grs. water.

Total cap. brass wheel = cap. 1800 grs. water.

* This increase of temperature was, it is necessary to observe, a mixed quantity, depending partly upon the friction of the water, and partly upon the friction of the vertical axis of the apparatus upon its pivot and bearing, *c c*, fig. 1. The latter source of heat was however only equal to about $\frac{1}{10}$th of the former. Similarly also, in the experiments on the friction of solids hereafter detailed, the cast-iron discs revolving in mercury, rendered it impossible to avoid a very small degree of friction among the particles of that fluid. But since it was found that the quantity of heat evolved was the same, for the same quantity of force expended, in both cases, *i. e.* whether a minute quantity of heat arising from friction of solids was mixed with the heat arising from the friction of a fluid, or whether, on the other hand, a minute quantity of heat arising from the friction of a fluid was mingled with the heat developed by the friction of solids, I thought there could be no impropriety in considering the heat as if developed from a simple source,—in the one case entirely from the friction of a fluid, and in the other entirely from the friction of a solid body.

† The washer, weighing only 38 grs., was reckoned as copper in this estimate. ‡ Ann. de Ch. 1841, t. i.

The capacity of a brass stopper which was placed in the neck *b*, fig. 3, for the purpose of preventing the contact of air with the water as much as possible, was equal to that of 10·3 grs. of water: the capacity of the thermometer had not to be estimated, because it was always brought to the expected temperature before immersion. The entire capacity of the apparatus was therefore as follows:—

Water	93229·7
Copper as water. . .	2430·2
Brass as water . . .	1810·3
Total . .	97470·2

So that the total quantity of heat evolved was 0°·563209 in 97470·2 grs. of water, or, in other words, 1° Fahr. in 7·842299 lbs. of water.

The estimate of the force applied in generating this heat may be made as follows:—The weights amounted to 406152 grs., from which must be subtracted the friction arising from the pulleys and the rigidity of the string; which was found by connecting the two pulleys with twine passing round a roller of equal diameter to that employed in the experiments. Under these circumstances, the weight required to be added to one of the leaden weights in order to maintain them in equable motion was found to be 2955 grs. The same result, in the opposite direction, was obtained by adding 3055 grs. to the other leaden weight. Deducting 168 grs., the friction of the roller on its pivots, from 3005, the mean of the above numbers, we have 2837 grs. as the amount of friction in the experiments, which, subtracted from the leaden weights, leaves 403315 grs. as the actual pressure applied.

The velocity with which the leaden weights came to the ground, viz. 2·42 inches per second, is equivalent to an altitude of 0·0076 inch. This, multiplied by 20, the number of times the weights were wound up in each experiment, produces 0·152 inch, which, subtracted from 1260·248, leaves 1260·096 as the corrected mean height from which the weights fell.

This fall, accompanied by the above-mentioned pressure, represents a force equivalent to 6050·186 lbs. through one foot; and $0{\cdot}8464 \times 20 = 16{\cdot}928$ foot-lbs. added to it, for the force developed by the elasticity of the string after the weights had touched the ground, gives 6067·114 foot-pounds as the mean corrected force.

Hence $\frac{6067{\cdot}114}{7{\cdot}842299} = 773{\cdot}64$ foot-pounds, will be the force which, according to the above experiments on the friction of water, is equivalent to 1° Fahr. in a lb. of water.

2*nd Series of Experiments.*—Friction of Mercury. Weight of the leaden weights and string, 203026 grs. and 203073 grs. Velocity of the weights in descending, 2·43 inches per second. Time occupied by each experiment, 30 minutes. Thermometer for ascertaining the temperature of the mercury, C. Thermometer for registering the temperature of the air, B. Weight of cast iron apparatus, 68446 grs. Weight of mercury contained by it, 428292 grs.

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Table II.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
		°	°	°	°	
1 Friction.....	1265·42	58·491	1·452 +	58·780	61·107	2·327 gain
1 Radiation ...	0	58·939	2·056 +	61·107	60·884	0·223 loss
2 Radiation ...	0	58·390	0·237 —	58·119	58·188	0·069 gain
2 Friction.....	1265·77	58·949	0·467 +	58·188	60·644	2·456 gain
3 Friction.....	1265·73	57·322	1·203 +	57·325	59·725	2·400 gain
3 Radiation ...	0	57·942	1·678 +	59·725	59·515	0·210 loss
4 Radiation ...	0	57·545	0·010 —	57·518	57·553	0·035 gain
4 Friction.....	1264·72	58·135	0·624 +	57·553	59·965	2·412 gain
5 Friction.....	1265·73	57·021	0·907 +	56·715	59·141	2·426 gain
5 Radiation ...	0	57·596	1·474 +	59·141	58·999	0·142 loss
6 Radiation ...	0	56·406	0·174 +	56·565	56·595	0·030 gain
6 Friction.....	1265·65	57·057	0·749 +	56·595	59·017	2·422 gain
7 Friction.....	1269·55	58·319	0·049 +	57·115	59·622	2·507 gain
7 Radiation ...	0	58·771	0·831 +	59·622	59·583	0·039 loss
8 Radiation ...	0	60·363	0·612 —	59·691	59·811	0·120 gain
8 Friction.....	1257·70	60·842	0·209 +	59·811	62·292	2·481 gain
9 Friction.....	1255·77	60·282	1·044 +	60·129	62·524	2·395 gain
9 Radiation ...	0	60·862	1·576 +	62·524	62·352	0·172 loss
10 Friction.....	1255·33	60·725	0·764 +	60·266	62·713	2·447 gain
10 Radiation ...	0	61·340	1·313 +	62·713	62·593	0·120 loss
11 Radiation ...	0	58·654	0·109 +	58·755	58·772	0·017 gain
11 Friction.....	1266·47	59·234	0·746 +	58·772	61·189	2·417 gain
12 Radiation ...	0	56·436	0·247 +	56·673	56·694	0·021 gain
12 Friction.....	1265·80	57·240	0·673 +	56·694	59·133	2·439 gain
13 Friction.....	1264·70	55·002	1·808 +	55·638	57·982	2·344 gain
13 Radiation ...	0	55·633	2·213 +	57·982	57·711	0·271 loss
14 Friction.....	1265·20	54·219	1·273 +	54·290	56·694	2·404 gain
14 Radiation ...	0	54·595	1·972 +	56·694	56·441	0·253 loss
15 Radiation ...	0	53·476	0·174 +	53·633	53·667	0·034 gain
15 Friction.....	1265·63	53·995	0·872 +	53·667	56·067	2·400 gain
16 Radiation ...	0	52·082	0·254 +	52·332	52·341	0·009 gain
16 Friction.....	1265·45	52·479	1·047 +	52·341	54·711	2·370 gain
17 Friction.....	1257·50	50·485	1·453 +	50·772	53·105	2·333 gain
17 Radiation ...	0	50·821	2·164 +	53·105	52·865	0·240 loss
18 Radiation ...	0	48·944	0·450 —	48·434	48·554	0·120 gain
18 Friction.....	1257·50	49·330	0·462 +	48·554	51·031	2·477 gain
19 Friction.....	1257·50	48·135	1·273 +	48·219	50·598	2·379 gain
19 Radiation ...	0	48·725	1·780 +	50·598	50·413	0·185 loss
20 Radiation ...	0	48·878	0·148 —	48·687	48·773	0·086 gain
20 Friction.....	1257·50	49·397	0·597 +	48·773	51·216	2·443 gain
Mean Friction	1262·731	.....	0·8836+	.....	.....	2·41395 gain
Mean Radiation	0	.....	0·8279+	.....	.....	0·06570 loss
1	2	3	4	5	6	7

From the above Table, it appears that the effect of each degree of difference between the temperature of the laboratory and that of the apparatus was $0^{\circ}\cdot13\dot{7}42$. Hence $2^{\circ}\cdot41395+0^{\circ}\cdot0657+0^{\circ}\cdot007654=2^{\circ}\cdot487304$, will be the proximate value of the increase of temperature in the experiments. The further correction on account of the mean temperature of the apparatus in the friction experiments having been in reality $0^{\circ}\cdot028484$ higher than is indicated by the table, will be $0^{\circ}\cdot003914$, which, added to the proximate result, gives $2^{\circ}\cdot491218$ as the true thermometrical effect of the friction of the mercury.

In order to obtain the absolute quantity of heat evolved, it was requisite to ascertain the capacity for heat of the apparatus. I therefore caused it to be suspended by iron wire from a lever so contrived that the apparatus could be moved with rapidity and ease to any required position. The temperature of the apparatus having then been raised about 20°, it was placed in a warm air-bath, in order to keep its temperature uniform for a quarter of an hour, during which time the thermometer C, immersed in the mercury, was from time to time observed. The apparatus was then rapidly immersed into a thin copper vessel containing 141826 grs. of distilled water, the temperature of which was repeatedly observed by thermometer A. During the experiment the water was repeatedly agitated by a copper stirrer; and every precaution was taken to keep the surrounding atmosphere in a uniform state, and also to prevent the disturbing effects of radiation from the person of the experimenter. In this way I obtained the following results:—

	Time of observation.	Temperature of water.	Temperature of apparatus.
	′	°	°
Apparatus in air-bath	0	47·705	70·518
	5	47·705	70·492
	10	47·713	70·518
Instant of immersion	11		
Apparatus immersed in water	13½	49·836	57·673
	16	50·493	52·641
	21	50·694	50·941
	26	50·690	50·778
	31	50·667	50·744
	36	50·636	50·709

By applying the correction to the temperature of the water due to its observed increase during the first ten minutes of the experiment, and the still smaller correction due to the rise of the water in the can covering 60 square inches of copper at the temperature of the atmosphere, $47^{\circ}\cdot714$ was found to be the temperature of the water at the instant of immersion. To remove the apparatus from the warm air-bath, and to immerse it into the water, occupied only 10″, during which it must (according to preliminary experiments) have cooled $0^{\circ}\cdot027$. The heating effect of the air-bath

during the remaining 50″ (estimated from the rate of increase of temperature between the observations at 5′ and 10′) will be 0°·004. These corrections, applied to 70°·518, leave 70°·495 as the temperature of the apparatus at the moment of immersion.

The temperature of the apparatus at 26′ was 50°·778, indicating a loss of 19°·717. That of the water at the same time of observation, being corrected for the effect of the atmosphere (deduced from the observations of the cooling from 26′ to 36′ and of the heating from 0′ to 10′), will be 50°·777, indicating a gain of 3°·063. Twenty such results, obtained in exactly the same manner, are collected in the following Table.

TABLE III.

No.	Corrected temperature of water.		Gain of heat by the water.	Corrected temperature of apparatus.		Loss of heat by the apparatus.
	Commencement of experiment.	Termination of experiment.		Commencement of experiment.	Termination of experiment.	
1	47°·714	50°·777	3°·063	70°·495	50°·778	19°·717
2	48·127	51·113	2·986	70·518	51·147	19·371
3	48·453	51·430	2·977	70·642	51·452	19·190
4	47·543	50·598	3·055	70·674	50·684	19·990
5	44·981	48·449	3·468	70·901	48·468	22·433
6	45·289	48·701	3·412	70·769	48·657	22·112
7	45·087	48·497	3·410	70·504	48·494	22·010
8	46·375	49·614	3·239	70·678	49·662	21·016
9	47·671	50·832	3·161	71·500	50·873	20·627
10	47·693	50·801	3·108	70·878	50·821	20·057
11	48·728	51·714	2·986	70·947	51·714	19·233
12	47·240	50·414	3·174	71·006	50·392	20·614
13	48·324	51·345	3·021	70·939	51·362	19·577
14	49·079	51·905	2·826	70·332	51·937	18·395
15	49·635	52·490	2·855	71·012	52·504	18·508
16	47·207	50·282	3·075	70·265	50·263	20·002
17	46·227	49·402	3·175	69·877	49·314	20·563
18	46·053	49·296	3·243	70·367	49·258	21·109
19	45·733	48·981	3·248	70·068	49·001	21·067
20	47·170	50·317	3·147	70·741	50·332	20·409
Mean...	.....	.....	3·13145	.....	.....	20·300

I did not consider these experiments on the capacity of the apparatus sufficiently complete, until I had ascertained the heat produced by the wetting of the surface of the iron vessel. For this purpose the following trials were made in a similar manner to the above, with the exception that the observations did not require to be extended beyond 26′.

TABLE IV.

No.	Corrected temperature of water.		Gain or loss of heat by water.	Corrected temperature of apparatus.		Gain or loss of heat by apparatus.
	Commencement of experiment.	Termination of experiment.		Commencement of experiment.	Termination of experiment.	
1	50°·558	50°·556	0°·002 loss	50°·565	50°·589	0°·024 gain
2	49·228	49·232	0·004 gain	49·239	49·254	0·015 gain
3	48·095	48·106	0·011 gain	48·034	48·099	0·065 gain
4	47·416	47·425	0·009 gain	47·384	47·429	0·045 gain
5	47·484	47·532	0·048 gain	48·103	47·782	0·321 loss
6	47·429	47·439	0·010 gain	47·703	47·610	0·093 loss
7	47·624	47·637	0·013 gain	47·870	47·790	0·080 loss
8	47·705	47·712	0·007 gain	47·915	47·859	0·056 loss
9	47·685	47·702	0·017 gain	47·891	47·837	0·054 loss
10	48·733	48·793	0·060 gain	49·498	49·112	0·386 loss
11	49·689	49·694	0·005 gain	49·946	49·842	0·104 loss
12	48·191	48·168	0·023 loss	47·972	48·134	0·162 gain
13	48·101	48·119	0·018 gain	48·310	48·254	0·056 loss
14	49·413	49·390	0·023 loss	49·249	49·413	0·164 gain
15	49·243	49·241	0·002 loss	49·343	49·318	0·025 loss
16	49·103	49·103	0	49·172	49·172	0
17	46·991	46·902	0·089 loss	46·204	46·923	0·719 gain
18	46·801	46·814	0·013 gain	47·139	46·953	0·186 loss
19	46·624	46·624	0	46·652	46·652	0
20	46·266	46·158	0·108 loss	45·369	46·167	0·798 gain
Mean...	.....	.....	0·0016 loss	.....	.....	0·03155 gain

By adding these results to those of the former table, we have a gain of temperature in the water of 3°·13305, and a loss in the apparatus of 20°·33155. Now the capacity of the can of water was estimated as follows:—

Water	141826 grs.
15622 grs. copper as water . .	1486 grs.
Thermometer and stirrer as water	118 grs.
Total	143430 grs.

Hence $\frac{3{\cdot}13305}{20{\cdot}33155} \times 143430 = 22102{\cdot}27$, the capacity of the apparatus as tried. The addition of 21·41 (the capacity of 643 grs. of mercury which had been removed in order to admit of the expansion of 70°) to, and the substraction of 52 grs. (the capacity of the bulb of thermometer C, and of the iron wire employed in suspending the apparatus) from this result, leaves 22071·68 grs. of water as the capacity of the apparatus employed in the friction of mercury.

The temperature 2°·491218 in the above capacity, equivalent to 1° in 7·85505 lbs. of water, was therefore the absolute mean quantity of heat evolved by the friction of mercury.

The leaden weights amounted to 406099 grs., from which 2857 grs., subtracted for the friction of the pulleys, leaves 403242 grs. The mean height from which they fell, as given in Table II., was 1262·731 inches, from which 0·152 inch, subtracted for the velocity of fall, leaves 1262·579 inches. This height, combined with the above weight, is equivalent to 6061·01 foot-lbs., which, increased by 16·929 foot-lbs. on account of the elasticity of the string, gives 6077·939 foot-lbs. as the mean force employed in the experiments.

$\frac{6077{\cdot}939}{7{\cdot}85505} = 773{\cdot}762$; which is therefore the equivalent derived from the above experiments on the friction of mercury. The next series of experiments were made with the same apparatus, using lighter weights.

3rd Series of Experiments.—Friction of Mercury. Weight of the leaden weights and string, 68442 grs. and 68884 grs. Velocity of the weights in descending, 1·4 inch per second. Time occupied by each experiment, 35 minutes. Thermometer for ascertaining the temperature of the mercury, C. Thermometer for registering the temperature of the air, B.

TABLE V.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
1 Friction.....	1292·12	49°·539	0°·399+	49°·507	50°·370	0°·863 gain
1 Radiation	0	50·165	0·226+	50·370	50·413	0·043 gain
2 Friction.....	1292·00	49·865	0·189+	49·606	50·503	0·897 gain
2 Radiation	0	50·363	0·159+	50·503	50·542	0·039 gain
3 Friction.....	1293·18	50·189	0·460+	50·168	51·030	0·862 gain
3 Radiation	0	50·617	0·408+	51·030	51·021	0·009 loss
4 Radiation	0	50·750	0·146+	50·873	50·920	0·047 gain
4 Friction.....	1293·25	51·401	0·013—	50·920	51·856	0·936 gain
5 Radiation	0	49·936	0·121+	50·031	50·083	0·052 gain
5 Friction.....	1294·92	50·551	0·020—	50·083	50·980	0·897 gain
6 Radiation	0	50·638	0·135+	50·752	50·795	0·043 gain
6 Friction.....	1294·43	51·172	0·065+	50·795	51·680	0·885 gain
7 Radiation	0	51·553	0·260—	51·237	51·349	0·112 gain
7 Friction.....	1294·07	52·194	0·371—	51·349	52·298	0·949 gain
8 Friction.....	1293·30	52·774	0·019—	52·298	53·212	0·914 gain
8 Radiation	0	53·029	0·204+	53·212	53·255	0·043 gain
9 Friction.....	1294·05	51·513	0·306+	51·379	52·259	0·880 gain
9 Radiation	0	52·093	0·177+	52·259	52·281	0·022 gain
10 Friction.....	1293·95	51·197	0·180+	50·907	51·847	0·940 gain
10 Radiation	0	51·960	0·079—	51·847	51·916	0·069 gain
11 Friction.....	1292·80	50·577	0·652+	50·804	51·654	0·850 gain
11 Radiation	0	51·055	0·577+	51·654	51·611	0·043 loss
1	2	3	4	5	6	7

TABLE V. (Continued.)

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
12 Radiation	0	51·416	0·483 —	50·860	51·006	0·146 gain
12 Friction.....	1293·25	52·057	0·551 —	51·006	52·006	1·000 gain
13 Radiation	0	51·747	0·246 —	51·456	51·547	0·091 gain
13 Friction.....	1293·25	52·403	0·389 —	51·547	52·482	0·935 gain
14 Friction.....	1293·45	52·703	0·054 +	52·294	53·221	0·927 gain
14 Radiation	0	53·201	0·050 +	53·221	53·281	0·060 gain
15 Friction.....	1293·93	53·644	0·088 +	53·281	54·183	0·902 gain
15 Radiation	0	54·061	0·145 +	54·183	54·230	0·047 gain
16 Radiation	0	51·492	0·318 +	51·821	51·800	0·021 loss
16 Friction.....	1292·83	52·011	0·242 +	51·800	52·706	0·906 gain
17 Radiation	0	51·350	0·055 —	51·272	51·319	0·047 gain
17 Friction.....	1292·83	52·057	0·264 —	51·319	52·268	0·949 gain
18 Friction.....	1292·84	52·576	0·147 +	52·268	53·178	0·910 gain
18 Radiation	0	52·906	0·276 +	53·178	53·187	0·009 gain
19 Radiation	0	50·119	0·142 —	49·928	50·027	0·099 gain
19 Friction.....	1292·33	50·760	0·272 —	50·027	50·950	0·923 gain
20 Friction.....	1293·01	51·004	0·147 —	50·370	51·345	0·975 gain
20 Radiation	0	51·798	0·385 —	51·345	51·482	0·137 gain
21 Radiation	0	52·194	0·646 —	51·482	51·615	0·133 gain
21 Friction.....	1292·83	52·383	0·298 —	51·615	52·555	0·940 gain
22 Friction.....	1292·33	50·389	0·374 +	50·332	51·195	0·863 gain
22 Radiation	0	50·958	0·239 +	51·195	51·199	0·004 gain
23 Radiation	0	51·218	0·498 —	50·636	50·804	0·168 gain
23 Friction.....	1294·69	51·848	0·546 —	50·804	51·800	0·996 gain
24 Friction.....	1294·33	50·582	0·286 +	50·435	51·302	0·867 gain
24 Radiation	0	51·223	0·092 +	51·302	51·328	0·026 gain
25 Radiation	0	51·665	0·406 —	51·190	51·328	0·138 gain
25 Friction.....	1294·33	52·281	0·464 —	51·328	52·306	0·978 gain
26 Friction.....	1294·34	52·652	0·105 +	52·306	53·208	0·902 gain
26 Radiation	0	52·957	0·259 +	53·208	53·225	0·017 gain
27 Friction.....	1293·83	49·463	0·277 +	49·293	50·188	0·895 gain
27 Radiation	0	50·068	0·142 +	50·188	50·233	0·045 gain
28 Radiation	0	48·420	0·145 +	48·537	48·593	0·056 gain
28 Friction.....	1294·33	49·132	0·093 —	48·593	49·486	0·893 gain
29 Friction.....	1294·84	49·142	0·092 +	48·773	49·696	0·923 gain
29 Radiation	0	49·783	0·053 —	49·696	49·765	0·069 gain
30 Radiation	0	50·251	0·422 —	49·765	49·894	0·129 gain
30 Friction.....	1294·33	50·597	0·246 —	49·894	50·808	0·914 gain
Mean Friction ...	1293·532	.....	0·00743 +	.....	.....	0·9157 gain
Mean Radiation...	0	.....	0·0048 +	.....	.....	0·0606 gain
1	2	3	4	5	6	7

The effect of each degree of difference between the temperature of the laboratory and that of the apparatus being $0°{\cdot}18544$, $0°{\cdot}9157 - 0°{\cdot}0606 + 0°{\cdot}000488 = 0°{\cdot}855588$, will be the proximate mean increase of temperature in the above series of experiments. The correction, owing to the mean temperature of the mercury in the friction experiments being $0°{\cdot}013222$ higher than appears in the table, will be $0°{\cdot}002452$, which, being added to the proximate result, gives $0°{\cdot}85804$ as the true thermometrical effect. This, in the capacity of $22071{\cdot}68$ grs. of water, is equal to $1°$ in $2{\cdot}70548$ lbs. of water.

The leaden weights amounted to 137326 grs., from which 1040 grs. must be subtracted for the friction of the pulleys, leaving 136286 grs. as the corrected weight. The mean height of fall was $1293{\cdot}532$ inches, from which $0{\cdot}047$ inch, subtracted on account of the velocity with which the weights came to the ground, leaves $1293{\cdot}485$ inches. This fall, combined with the above corrected weight, is equivalent to $2098{\cdot}618$ foot-lbs., which, with $1{\cdot}654$ foot-lb., the force developed by the elasticity of the string, gives $2100{\cdot}272$ foot lbs. as the mean force employed in the experiments.

$\frac{2100{\cdot}272}{2{\cdot}70548} = 776{\cdot}303$, will therefore be the equivalent from the above series of experiments, in which the amount of friction of the mercury was moderated by the use of lighter weights.

4th Series of Experiments.—Friction of Cast Iron. Weight of cast iron apparatus, 44000 grs. Weight of mercury contained by it, 204355 grs. Weight of the leaden weights and string attached, 203026 grs. and 203073 grs. Average velocity with which the weights fell, $3{\cdot}12$ inches per second. Time occupied by each experiment, 38 minutes. Thermometer for ascertaining the temperature of the mercury, C. Thermometer for registering the temperature of the air, A.

Table VI.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
		°	°	°	°	°
1 Friction.....	1257·90	46·362	2·544 +	46·837	50·976	4·139 gain
1 Radiation	0	46·648	3·950 +	50·976	50·220	0·756 loss
2 Radiation	0	47·296	0·455 —	46·730	46·953	0·223 gain
2 Friction.....	1258·97	47·891	1·247 +	46·953	51·323	4·370 gain
3 Friction.....	1261·80	47·705	1·830 +	47·352	51·718	4·366 gain
3 Radiation	0	48·547	2·950 +	51·718	51·276	0·442 loss
4 Radiation	0	47·825	0·044 —	47·756	47·807	0·051 gain
4 Friction.....	1260·35	48·385	1·598 +	47·807	52·160	4·353 gain
5 Radiation	0	48·323	0·248 —	48·009	48·142	0·133 gain
5 Friction.....	1260·15	48·833	1·494 +	48·142	52·513	4·371 gain
6 Friction.....	1259·95	48·049	1·995 +	47·902	52·186	4·284 gain
6 Radiation	0	48·632	3·283 +	52·186	51·645	0·541 loss
7 Radiation	0	50·385	0·240 —	50·053	50·237	0·184 gain
7 Friction.....	1263·13	51·018	1·408 +	50·237	54·616	4·379 gain
8 Friction.....	1262·12	48·385	1·096 +	47·249	51·714	4·465 gain
8 Radiation	0	49·199	2·343 +	51·714	51·371	0·343 loss
9 Friction.....	1257·20	49·721	2·495 +	50·160	54·273	4·113 gain
9 Radiation	0	50·338	3·643 +	54·273	53·689	0·584 loss
10 Radiation	0	48·439	0·821 +	49·271	49·250	0·021 loss
10 Friction.....	1258·70	49·690	2·282 +	49·877	54·067	4·190 gain
Mean Friction ...	1260·027	.....	1·7989+	.....	.....	4·303 gain
Mean Radiation...	0	.....	1·6003+	.....	.....	0·2096 loss
1	2	3	4	5	6	7

From the above Table, it appears that there was a thermometrical effect of 0°·20101 for each degree of difference between the temperature of the laboratory and that of the apparatus. Hence $4°{\cdot}303+0°{\cdot}2096+0°{\cdot}03992=4°{\cdot}55252$, will be the proximate mean increase of temperature. The correction, owing to the mean temperature of the mercury in the friction experiments appearing 0°·07625 too low in the table, will be 0°·01533, which, added to the proximate result, gives 4°·56785 as the true mean increase of temperature.

The capacity of the apparatus was obtained by experiments made in precisely the same manner that I have already described in the case of the mercurial apparatus for fluid friction. Their results are collected into the following Table.

Table VII.

No.	Corrected temperature of water.		Gain of heat by the water.	Corrected temperature of apparatus.		Loss of heat by the apparatus.
	Commencement of experiment.	Termination of experiment.		Commencement of experiment.	Termination of experiment.	
	°	°	°	°	°	°
1	45·535	47·305	1·770	71·112	47·421	23·691
2	46·210	47·937	1·727	71·292	48·073	23·219
3	47·334	49·023	1·689	71·454	49·151	22·303
4	49·007	50·555	1·548	71·152	50·632	20·520
5	47·895	49·498	1·603	71·249	49·636	21·613
6	48·784	50·357	1·573	71·445	50·460	20·985
7	50·323	51·757	1·434	70·793	51·808	18·985
8	47·912	49·525	1·613	71·253	49·653	21·600
9	48·449	50·013	1·564	70·798	50·083	20·715
10	49·836	51·337	1·501	71·356	51·375	19·981
11	46·870	48·559	1·689	71·026	48·657	22·369
12	48·562	50·151	1·589	71·291	50·199	21·092
Mean...	.....	.....	1·60833	.....	.....	21·42275

By adding 0°·00071 and 0°·0141, the loss and gain of Table IV. reduced to the surface of the solid-friction apparatus, to the above mean results, we have a gain of 1°·60904 by the water and a loss of 21°·43685 by the apparatus. The capacity of the can of water was in this instance as follows:—

Water	155824 grs.
Copper can as water	1486 grs.
Thermometer and stirrer as ditto	118 grs.
Total . . .	157428 grs.

Hence $\frac{1{\cdot}60904}{21{\cdot}43685} \times 157428 = 11816{\cdot}47$, will be the capacity of the apparatus as tried. By applying the two corrections, one additive on account of the absence during the trials of 300 grs. of mercury, the other subtractive on account of the capacity of the thermometer C and suspending wire, we obtain 11796·07 grs. of water as the capacity of the apparatus during the experiments.

The temperature 4°·56785 in the above capacity, equivalent to 1° in 7·69753 lbs. of water, was therefore the mean absolute quantity of heat evolved by the friction of cast iron.

The leaden weights amounted to 406099 grs., from which 2857 grs., subtracted on account of the friction of the pulleys, leaves 403242 grs. as the pressure applied to the apparatus.

Owing to the friction being in the simple ratio of the velocity, it required a good deal of practice to hold the regulating lever so as to cause the weights to descend to

the ground with anything like a uniform and moderate velocity. Hence, although the mean velocity was 3·12 inches per second, the force with which the weights struck the ground could not be correctly estimated by that velocity as in the case of fluid friction. However, it was found that the noise produced by the impact was on the average equal to that produced by letting the weights fall from the height of one-eighth of an inch. It generally happened also that in endeavouring to regulate the motion, the weights would stop suddenly before arriving at the ground. This would generally happen once, sometimes twice, during the descent of the weights, and I estimate the force thereby lost as equal to that lost by impact with the ground. Taking therefore the total loss at one-fourth of an inch in each fall, we have twenty times that quantity, or 5 inches, as the entire loss, which, subtracted from 1260·027, leave 1255·027 inches as the corrected height through which the weight of 403242 grs. operated. These numbers are equivalent to 6024·757 foot-lbs., and adding 16·464 foot-lbs. for the effect of the elasticity of the string, we have 6041·221 foot-lbs. as the force employed in the experiments.

The above force was not however entirely employed in generating heat in the apparatus. It will be readily conceived that the friction of a solid body like cast iron must have produced a considerable vibration of the framework upon which the apparatus was placed, as well as a loud sound. The value of the force absorbed by the former was estimated by experiment at 10·266 foot-lbs. The force required to vibrate the string of a violoncello, so as to produce a sound which could be heard at the same distance as that arising from the friction, was estimated by me, with the concurrence of another observer, at 50 foot-lbs. These numbers, subtracted from the previous result, leave 5980·955 foot-lbs. as the force actually converted into heat. $\frac{5980\cdot955}{7\cdot69753}=776\cdot997$, will therefore be the equivalent derived from the above experiments on the friction of cast iron. The next series of experiments was made with the same apparatus, using lighter weights.

5th Series of Experiments.—Friction of Cast Iron. Weight of leaden weights, 68442 grs. and 68884 grs. Average velocity of fall, 1·9 inch per second. Time occupied by each experiment, 30 minutes. Thermometer for ascertaining the temperature of the mercury, C. Thermometer for registering the temperature of the laboratory, A.

TABLE VIII.

No. of experiment and cause of change of temperature.	Total fall of weights in inches.	Mean temperature of air.	Difference between mean of columns 5 and 6 and column 3.	Temperature of apparatus.		Gain or loss of heat during experiment.
				Commencement of experiment.	Termination of experiment.	
		°	°	°	°	°
1 Friction.....	1281·07	47·404	0·852 +	47·494	49·018	1·524 gain
1 Radiation	0	48·003	0·998 +	49·018	48·984	0·034 loss
2 Radiation	0	48·269	0·702 +	48·984	48·958	0·026 loss
2 Friction.....	1280·74	48·516	1·189 +	48·958	50·452	1·494 gain
3 Radiation	0	49·003	0·133 −	48·812	48·928	0·116 gain
3 Friction.....	1285·10	49·728	0·022 +	48·928	50·572	1·644 gain
4 Friction.....	1283·89	50·138	1·172 +	50·572	52·049	1·477 gain
4 Radiation	0	50·408	1·581 +	52·049	51·929	0·120 loss
5 Friction.....	1282·45	46·798	0·558 +	46·554	48·159	1·605 gain
6 Friction.....	1281·29	47·296	1·571 +	48·159	49·576	1·417 gain
5 Radiation	0	47·535	1·929 +	49·576	49·353	0·223 loss
6 Radiation	0	47·651	1·607 +	49·353	49·164	0·189 loss
7 Radiation	0	46·261	0·298 −	45·880	46·047	0·167 gain
8 Radiation	0	46·748	0·617 −	46·047	46·215	0·168 gain
7 Friction.....	1276·07	46·810	0·978 +	47·022	48·554	1·532 gain
8 Friction.....	1275·17	47·366	1·883 +	48·554	49·945	1·391 gain
9 Radiation	0	46·771	0·271 −	46·425	46·575	0·150 gain
9 Friction.....	1276·95	47·126	0·258 +	46·575	48·194	1·619 gain
10 Friction.....	1276·84	47·238	1·655 +	48·194	49·593	1·399 gain
10 Radiation	0	47·335	2·142 +	49·593	49·361	0·232 loss
Mean Friction ...	1279·957	.....	1·0138 +	.....	.....	1·5102 gain
Mean Radiation...	0	.....	0·764 +	.....	.....	0·0223 loss
1	2	3	4	5	6	7

From the above Table, it appears that the effect of each degree of difference between the temperature of the laboratory and that of the apparatus was 0°·1591. Hence $1°{\cdot}5102+0°{\cdot}0223+0°{\cdot}03974=1°{\cdot}57224$, will be the proximate heating effect. To this the addition of 0°·00331, on account of the mean temperature of the apparatus in the friction experiments having been in reality 0°·02084 higher than appears in the Table, gives the real increase of temperature in the experiments at 1°·57555, which, in the capacity of 11796·07 grs. of water, is equivalent to 1° in 2·65504 lbs. of water.

The leaden weights amounted to 137326 grs., from which 1040 grs., subtracted for the friction of the pulleys, leaves 136286 grs. The velocity of descent, which was in this case much more easily regulated than when the heavier weights were used, was 1·9 inch per second. Twenty impacts with this velocity indicate a loss of fall of 0·094 inch, which, subtracted from 1279·957, leaves 1279·863 inches as the corrected height from which the weights fell.

The above height and weight are equivalent to 2076·517 foot-lbs., to which the addition of 1·189 foot-lb. for the elasticity of the string, gives 2077·706 foot-lbs. as the

total force applied. The corrections for vibration and sound (deduced from the data obtained in the last series, on the hypothesis that they were proportional to the friction by which they were produced) will be 3·47 and 16·9 foot-lbs. These quantities, subtracted from the previous result, leave 2057·336 foot-lbs. as the quantity of force converted into heat in the apparatus.

$\frac{2057{\cdot}336}{2{\cdot}65504}=774{\cdot}88$, will therefore be the equivalent as derived from this last series of experiments.

The following Table contains a summary of the equivalents derived from the experiments above detailed. In its fourth column I have supplied the results with the correction necessary to reduce them to a vacuum.

TABLE IX.

No. of series.	Material employed.	Equivalent in air.	Equivalent in vacuo.	Mean.
1	Water	773·640	772·692	772·692
2	Mercury	773·762	772·814	774·083
3	Mercury	776·303	775·352	
4	Cast iron.....	776·997	776·045	774·987
5	Cast iron.....	774·880	773·930	

It is highly probable that the equivalent from cast iron was somewhat increased by the abrasion of particles of the metal during friction, which could not occur without the absorption of a certain quantity of force in overcoming the attraction of cohesion. But since the quantity abraded was not considerable enough to be weighed after the experiments were completed, the error from this source cannot be of much moment. I consider that 772·692, the equivalent derived from the friction of water, is the most correct, both on account of the number of experiments tried, and the great capacity of the apparatus for heat. And since, even in the friction of fluids, it was impossible entirely to avoid vibration and the production of a slight sound, it is probable that the above number is slightly in excess. I will therefore conclude by considering it as demonstrated by the experiments contained in this paper,—

1st. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of force expended.* And,

2nd. *That the quantity of heat capable of increasing the temperature of a pound of water* (*weighed* in vacuo, *and taken at between* 55° *and* 60°) *by* 1° FAHR., *requires for its evolution the expenditure of a mechanical force represented by the fall of* 772 *lbs. through the space of one foot.*

Oak Field, near Manchester,
June 4th, 1849.

IV. *On the Automatic Registration of Magnetometers, and Meteorological Instruments, by Photography.—No. III.* By Charles Brooke, *M.B., F.R.S.*

Received June 21,—Read June 21, 1849.

On the Construction of the Self-registering Thermometer Apparatus.

In my second paper on Automatic Registration*, the means of obtaining a photographic register of the variations of the thermometer were briefly mentioned, and in the annexed plate a specimen was given of the register thus obtained; but as an apparatus possessing the requisites for practical application had not then been constructed, it may not be undesirable to those who are interested in the advancement of meteorological science, to know the means by which this object has been accomplished. A vertical revolving cylinder, and the carrying time-piece described in the above paper (see Plate VI. figs. 4, 5, 6, 7, 8), are mounted on a stand measuring 30 inches by 12, supported by four legs; the stems of the thermometer and psychrometer pass up through the table, and between the lenses and the adjacent surfaces of the cylinder; and the long cylindrical bulbs are sufficiently below the stand to be freely influenced by the currents of air, and at the same time to remain wholly unaffected by the heat of the lamps which are placed on wooden supports at each end of the stand, at such a height that the flame may be opposite the middle of the photographic paper on the cylinder.

As it is impossible to superpose two registers of these instruments on the same paper, which may be done without inconvenience when the indication consists in a dark line, as in the photographs of the barometer and the magnetometers, the time-piece is so constructed that the hour-hand makes half a revolution in twenty-four hours. By this arrangement the two halves of the paper surrounding the cylinder give respectively a perfect diary of the two instruments. The glass cylinder is covered by a concentric cylindrical zinc case, having slits on opposite sides corresponding to the stems of the instruments, which are capable of being closed by sliding doors; by these means the cylinder, protected by its case, may be carried to or from the room in which the photographic manipulations are conducted, without any risk of exposure to light. The whole apparatus is also covered by a wind- and water-tight zinc case which rests on the stand, and is divided into separate compartments for the lamps by a partition towards each end, for the purpose of more completely isolating the thermometers from the heat produced by their combustion.

The cylindrical arrangement above described, so obviously desirable in enabling

* See Philosophical Transactions, 1847, Part I.

the two thermometric instruments to be registered by one apparatus and on one piece of paper, was at first open to a grave objection, which has however subsequently been entirely removed. The pencil of rays incident on the stem of the thermometer must necessarily be a fan-shaped pencil, by the oblique rays of which the points corresponding to each degree would not be transferred to the respectively opposite points of the paper. If the surface of the cylinder were always parallel to, and equidistant from, the stem of the thermometer, this distortion of the scale would be constant and uniform, and therefore readily estimated; but from the unavoidable imperfections in form and variations in size of the different cylinders employed, it would be extremely difficult to estimate correctly the distortion of the scale, and hence to infer the true temperature from the register. And this uncertainty would have been especially felt at very low temperatures, when the place of the mercury is impressed by the most oblique rays on the paper, and when small errors of relative temperature would largely affect the deduced hygrometric condition of the atmosphere. This difficulty has been obviated by enabling the apparatus to print continuously the scale of the thermometers, as well as to indicate the position of the mercury. This has been effected by placing fine wires, opposite to each degree, across the aperture in the scale frame, through which the light is transmitted to the stem of the instrument. By these wires a minute portion of the exposed paper is protected from light, and thus the darkened portion of the register is traversed by a series of parallel lines, corresponding with the scale of the thermometer. In order to remove any ambiguity in the reading of this scale, a coarser wire is placed at every ten degrees, and an additional coarse wire at the points 32°, 54°, 76° and 98°; as one of these points may always be made to appear on the register, the relative position of the extra coarse wire will determine the point of the scale which it represents.

It may here be mentioned that the wet bulb, although more than 6 inches in length, is kept perfectly saturated by being moistened at three different points by small bundles of lamp-cotton placed round the muslin covering of the bulb, and immersed in a vessel of water placed nearly opposite its middle point.

It is very evident that the apparatus must afford some ready method of marking the time-scale on the paper, that is, of identifying any given epoch of time with the indications of the register: this is effected by closing at any two known times the sliding doors of the cylindrical case, for five minutes, and then re-opening them. Two undarkened lines will be observed on the paper, corresponding to the known times; the intervening space being subdivided by the elastic scale, the time-scale is rendered complete*.

It may also be remarked, that in all the other photographic registers obtained at the Royal Observatory by the instruments previously described, the only certain method of marking the time-scale is found to consist in breaking the continuity of the line at a known epoch: this is effected by a piece of brass similar to one side of a

* As a facsimile of a photographic diurnal register will be found in the Greenwich Magnetical and Meteorological Observations for 1837, it is unnecessary to introduce it in this place.

parallel ruler, placed edgewise, one of the connecting pieces being prolonged and passing down through the stand to act as a lever, by which the parallel moving piece is raised between the cylindrical lens and the cone of the cylinder, so as to intercept the pencil of light which traces the register line. The light is usually excluded for 5^m, admitted for 1^m, again excluded for 5^m, and then re-admitted, the times of exclusion, admission and re-admission being recorded. If, during the second passage of the tracing pencil of light over the paper, a break of six or eight minutes be made, without the intervening spot, it will be found a convenient method of distinguishing the two lines, in case of any ambiguity.

The scales of the thermometers in use have about 8° to 1 inch, from the registers of which the temperature may be readily read with certainty to less than a tenth of a degree. Of this scale, a space of about 60° may be illuminated at one time; and in order that the temperature indicated may always be within the field, the thermometers are capable of being raised or lowered by a screw, so as to bring the mean temperature of the season nearly opposite the middle of the paper: thus there is no probability that the record of any unusual and extreme changes of temperature will be lost.

In the description of the camphine lamp given in the first paper, previously referred to, the wick was stated to have been placed below the diaphragm in the chimney; it has since been found that there is another position in which equally perfect combustion takes place, which is when the wick is raised to about an equal distance above the diaphragm; with this position of the wick, the liability to smoke is very materially diminished.

Equally good effects have recently been produced by gas, saturated with the vapour of coal naphtha, which renders the light much whiter and more intense. Without this addition to the gas the photographic paper is feebly affected during periods of rapid movement of the magnet. The light used is that of a small fish-tail burner, so made as to spread the gas as much as possible; the flame is placed edgewise towards the mirror, in which position the illumination of the mirror is the brightest.

The employment of these instruments is not however limited to localities in which either camphine or gas is accessible; for the barometer and thermometers, in which large and rapid movements of the tracing pencil of light are never required to be depicted, an oil-lamp will answer sufficiently well: and by the same means the ordinary diurnal variations of the magnetometers may be delineated; but no opportunity has yet occurred of obtaining, by means of an oil-lamp, a register of the rapid movements occurring during a considerable disturbance.

On a New Method of determining the Scale and Temperature Coefficients of Magnets used in observing the Changes of Magnetic Force.

It appears from the ordinary formula expressing the equilibrium of the bifilar magnet, that small changes in the amount of horizontal force will have the same effect in displacing the magnet, as small corresponding changes in the suspended weight. Having then carefully weighed the magnet, the mirror and the suspending frame, two

small weights have been made, each equal to the $\frac{1}{1000}$th part of the whole weight. While the register is in action, one of these weights is placed on the torsion circle, and at an interval of time equal to that of one oscillation of the magnet, the second is added: if this be carefully done, the magnet will be very nearly at rest in its new position. After half an hour, or any convenient interval of time, the weights are removed in the same manner; and this must be repeated sufficiently often to eliminate the error of reading by a finely divided scale the displacement of the register line. Half the scale reading of this displacement may therefore be taken as the value of 0·001 of the whole horizontal force. By this process the necessity of making several accurate linear measurements of the apparatus, and the errors that might arise therefrom, are avoided.

The following is the proposed method of determining the temperature coefficient. Let two magnets, one of them having a known coefficient, and that of the other to be now determined, be suspended in the bifilar method, at a distance of 15 feet from each other, the line joining their centres being a normal to the plane of the magnetic meridian. The torsion of the double threads should be in opposite directions, so that when the magnets are duly adjusted in equilibrium, in the line joining their centres, the similar poles may be towards each other.

The most convenient scale coefficient of the bifilar magnet, for the purpose of photographic registration, appears to be that which renders the angular value of the ordinary diurnal range nearly equal to the range of the declination magnet; the pulley over which the suspension thread of what may be called the standard magnet passes, being made of such a size as to give the required value to its scale coefficient, the distance between the threads of the other or trial magnet may be conveniently adjusted by a right- and left-handed screw (as in the suspension frame described in a former paper), so as to give a nearly equal value to its scale coefficient. The previously described arrangements for photographic registration being made, the registering apparatus is placed midway between the magnets, and by a few trials, the ratio of its distances from the magnets may be so arranged as to make their scale coefficients exactly equal. The magnets, having been previously protected by a coat of varnish, are suspended in water. The vessel made use of is a double zinc trough or box, the inner one being 18 inches long, 2 inches wide, and 4 inches deep, the outer one 3 inches longer and wider, leaving an equal space on all sides between the two, and half an inch deeper, with separate covers to each. For the standard magnet, the inner box only should be filled with water, the intervening space of air between the two tending to retard any variation of temperature of the water. For raising the temperature of the trial magnet, the outer box should be filled with warm water at such a temperature as will raise the water in the inner box to about 100° Fahr. For lowering it to 32° Fahr., the outer box, or rather the space between the two, should be filled with a freezing mixture. The whole being allowed to cool gradually in the one case, and in the other to be raised gradually to the temperature of the atmosphere, the change of temperature will be found to be so slow, that the

temperature of the magnet may be presumed identical with that of the water in which it is immersed. This is ascertained by a thermometer with a long cylindrical bulb reaching nearly from the top to the bottom of the vessel, by which means it is presumed that the average temperature of the water will be most nearly determined.

These arrangements having been made, a simultaneous register of the two magnets is obtained, during the progress of which, the temperature of the magnets must be observed at recorded times, and at any convenient intervals of from a quarter of an hour to two or three hours, the intervals of observation being least at the highest and lowest temperatures of the trial magnet, when the change is most rapid. Having marked upon the register the epochs of observation, the differences between the changes of position of the lines at these points may be measured by a scale, and these differences will very accurately represent the scale-value of the changes of force due to the corresponding changes of temperature of the trial magnet; for ordinarily the temperature of the standard magnet may be considered constant during each of the intervals of observation.

A sufficient number of these differential scale-readings having been obtained, they may for reduction be conveniently arranged in five groups, between the temperatures 32°, 45°, 60°, 75°, 90°, 100°. Denoting the differences of temperature by D, the mean temperatures of the periods of observation by M, and the scale-readings by R, the mean temperature of each group is found from the formula $\frac{\Sigma(M \times D)}{\Sigma(D)}$, and the corresponding mean value of R for an interval of 1° Fahr. from the formula $\frac{\Sigma(D \times R)}{\Sigma(D^2)}$, which may be represented by ΔK, K being the temperature coefficient. As it has been found convenient to reduce magnetic observations to the temperature of 32° Fahr., let the excess of the above mean temperatures above that point be represented by t, and let x and y be the coefficients of the first and second powers of t in the value of K; then five equations will be obtained of the form

$$\Delta K = x + yt,$$

which being solved by the method of least squares, will give probably correct values of x and y. From the form of the preceding equation, it follows that

$$K = xt + \frac{1}{2}yt^2.$$

The above method has been applied to determine the temperature coefficients of two bar-magnets marked C.B. VIII. and C.B. IX*. But as the premises on which the observations were made present the usual obstacles of a dwelling-house to the free action of magnetic instruments, namely, the large mass of iron contained in the grates, only one position could be found in which the effects of the most contiguous masses of iron would nearly neutralize each other: and in consequence of this difficulty, the register of the trial-magnet here obtained has been compared with that obtained

* These magnets belong to a complete set of self-registering photographic apparatus intended to be presented to the Observatory at Cambridge by the Master of Trinity College.

simultaneously at the Royal Observatory; the result is therefore open to the objection of a *possible* difference in the changes of horizontal force at the two places. But it appears from a comparison of several photographic registers obtained simultaneously at Greenwich and in Keppel Street, some of which include periods of considerable disturbance, that a difference in the simultaneous changes of horizontal force in these two localities is very rarely perceptible.

The annexed Table contains the numerical observations from which the temperature coefficient of the bar C.B. VIII. has been determined. The scale-readings are taken

C.B. VIII.

Times of observation. March, 1849.	Scale-readings of Royal Observatory registers.	Differences.	Corresponding values on my scale. A×1·115.	Differences of my scale-readings.	Scale-readings of my registers.	Temperatures. Fahr.	Differences of temperature.	Mean temperatures.	Reduced scale-readings. B+C.	D².	D×R.	D×M.
d h m		A.	B.	C.			D.	M.	R.			
0 22 5	627				55	100·5						
30	630	3	3	80	135	95·2	5·3	97·9	83	2809	4399	51887
23 0	630	0	0	74	209	90·5	4·7	92·8	74	2209	3478	43616
30	628	− 2	− 2	54	263	87·3	3·2	88·9	52	1024	1664	28448
1 0 0	630	2	2	42	305	84·2	3·1	85·8	44	961	1364	26598
30	626	− 4	− 5	49	354	81·2	3·0	82·7	44	900	1320	24810
1 0	610	−16	−18	51	405	78·8	2·4	80·0	33	576	792	19200
2 4	610	0	0	89	494	73·4	5·4	76·1	89	2916	4806	41094
22 0	635				30	92·8						
30	639	4	5	78	108	88·4	4·4	90·6	83	1936	3652	39964
23 0	644	5	6	58	166	85·5	2·9	86·9	63	841	1827	25201
30	668	24	28	14	180	83·3	2·2	84·4	42	484	924	18568
2 0 0	660	− 8	− 9	58	238	80·4	2·9	81·8	49	841	1421	23722
1 0	652	− 8	− 9	83	321	75·8	4·6	78·1	74	2116	3404	35926
2 0	653	1	1	53	374	72·1	3·7	74·0	55	1369	2035	27380
3 0	646	− 7	− 8	54	428	68·9	3·2	70·5	46	1024	1472	22560
4 0	646	0	0	24	452	67·2	1·7	68·0	24	289	408	11560
5 10	621	−25	−29	57	509	65·3	1·9	66·2	28	361	532	12578
7 0	617	− 4	− 5	42	551	62·6	2·7	64·0	37	729	999	17280
11 38	608	− 9	−10	44	595	60·0	2·6	61·3	34	676	884	15938
20 19	601+16	9	10	21	616	58·0	2·0	59·0	31	400	620	11800
8 21 8	563				18	103·0						
34	572	9	10	74	92	98·5	4·5	100·8	84	2025	3780	45360
22 8	574	2	2	90	182	93·2	5·3	95·9	92	2809	4876	50827
48	596	22	25	58	240	88·5	4·7	90·8	83	2209	3901	42676
23 38	584	−12	−14	95	335	83·9	4·6	86·2	81	2116	3726	39652
9 0 3	556	−28	−32	63	398	81·8	2·1	82·8	31	441	651	17388
1 0	582	26	30	40	438	77·4	4·4	79·6	70	1936	3080	35024
2 25	562	−20	−23	103	541	72·6	4·8	75·0	80	2304	3840	36000
3 0	547	−15	−17	51	592	70·7	1·9	71·7	34	361	646	13623
30	560	13	15	16	608	69·4	1·3	70·1	31	169	403	9113
4 0	569	9	10	19	627	68·2	1·2	68·8	29	144	348	8256
5 7	573	4	4	30	657	66·7	1·5	67·5	34	225	510	10125
6 0	573	0	0	38	695	65·0	1·7	65·9	38	289	646	11203
40	576	3	3	24	719	63·7	1·3	64·4	27	169	351	8372
7 57	565	−11	−13	51	770	62·1	1·6	62·9	38	256	608	10064
9 9	568	3	3	15	785	60·8	1·3	61·4	18	169	234	7982
10 44	557+ 2	− 9	−10	22	807	59·6	1·2	66·2	12	144	144	7224
21 15	580+12	33	38	23	830	55·2	4·4	57·4	61	1936	2684	25256

C.B. VIII. (Continued.)

Times of observation. March, 1849.	Scale-readings of Royal Observatory registers.	Differences.	Corresponding values on my scale. A×1·115.	Differences of my scale-readings.	Scale-readings of my registers.	Temperatures. Fahr.	Differences of temperature.	Mean temperatures.	Reduced scale-readings. B+C.	D².	D×R.	D×M.
d h m		A.	B.	C.			D.	M.	R.			
10 1 42	600				195	33·5						
2 0	597	3	3	5	190	34·1	0·6	33·8	8	36	48	2028
2 30	589	8	9	6	184	35·2	1·1	34·6	15	121	165	3806
3 0	572	17	20	−1	185	36·8	1·6	36·0	19	256	304	5760
30	569	3	3	18	167	38·7	1·9	37·7	21	361	399	7163
4 0	569	0	0	20	147	40·4	1·7	39·5	20	289	340	6715
43	565	4	5	13	134	41·7	1·3	41·1	18	169	234	5343
5 38	567	− 2	− 2	22	112	42·8	1·1	42·3	20	121	220	4653
6 0	565	2	2	9	103	43·4	0·6	43·1	11	36	66	2586
7 13	557	8	9	13	90	44·8	1·4	44·1	22	196	308	6174
8 13	562	− 5	− 6	27	63	46·1	1·3	45·5	21	169	273	5915
9 9	571	− 9	−10	28	35	47·0	0·9	46·6	18	81	162	4194
43	565	6	7	1	34	47·5	0·5	47·3	8	25	40	2365
11 28	565	0	0	19	15	48·7	1·2	48·2	19	144	228	5784
11 6 40	550	− 1	− 1	36	92	69·8	2·3	68·6	35	529	805	15678
7 30	549	2	2	19	128	67·5	1·7	66·7	21	289	357	11339
8 8	551	− 4	− 5	31	147	65·8	2·0	64·8	26	400	520	12960
9 7	547	0	0	29	178	63·8	2·1	62·7	29	441	601	13167
10 21	547	0	0	12	207	61·7	0·9	61·2	12	81	108	5508
59	547				219	60·8						
11 23 45	614				654	33·2						
58	612	2	2	9	645	33·9	0·7	33·6	11	49	77	2352
12 0 20	608	4	5	14	631	35·4	1·5	34·6	19	225	285	5190
45	606	2	2	17	614	36·8	1·4	36·1	19	196	266	5084
1 0	596	10	11	3	611	37·8	1·0	37·3	14	100	140	3730
48	579	17	20	17	594	40·7	2·9	39·2	37	841	1073	11368
2 18	569	10	11	8	586	42·0	1·3	41·4	19	169	247	5382
3 0	579	−10	−11	33	553	43·5	1·5	42·8	22	225	330	6420
4 0	566	13	15	13	540	45·4	1·9	44·4	28	361	532	8436

on a scale having 100 divisions in an inch. The differences of the scale-readings of the Royal Observatory registers are reduced to the scale of the observed magnet by multiplying them by the ratio of the scale coefficients: this ratio is expressed by 1·115*. The reduced scale-readings, R, are the sums of the readings B and C, because the variation is represented in opposite directions on the two registers.

These quantities being arranged in five groups according to the temperatures M, and the mean values obtained by the above formulæ, the five following equations result:—

$$\begin{aligned} x+\ 7{\cdot}2y &= 13{\cdot}42 \\ x+21{\cdot}7y &= 14{\cdot}54 \\ x+34{\cdot}6y &= 15{\cdot}55 \\ x+49{\cdot}5y &= 16{\cdot}50 \\ x+62{\cdot}8y &= 17{\cdot}20 \end{aligned} \qquad \text{residual errors} \begin{cases} -0{\cdot}10 \\ +0{\cdot}02 \\ +0{\cdot}15 \\ +0{\cdot}08 \\ -0{\cdot}12 \end{cases}$$

* In the very few instances in which it appeared necessary, a correction has been applied to the Greenwich scale-readings for observed changes of temperature.

These equations, solved by the method of least squares, give

$$x=13{\cdot}0269\,; \quad y=0{\cdot}0685.$$

By the method of weights described above, the scale value of 0·001 of the total horizontal force was found to be 25·27 sc. div., consequently the values of x and y expressed in parts of force are

$$x=0{\cdot}00051550\,; \quad y=0{\cdot}000002710.$$

As the effect of a small increase of weight in displacing the magnet is the same as that of a small corresponding diminution of force, when the correction is subsequently applied to the magnet suspended in air, the value of x above found must be diminished by a small quantity representing the effect of the increase of weight due to the weight of the water displaced by the magnet being diminished by expansion, as the temperature increases; this may be called the coefficient of expansion, and may be thus found.

Let w, s, b be the cubical expansions of water, steel and brass respectively, for 1° Fahr., then

$$w=0{\cdot}0001500 \text{ (Ure)}$$
$$s=0{\cdot}0000204 \text{ (Smeaton)}$$
$$b=0{\cdot}0000291\,;$$

and if U be the weight lost by the magnet at 32° Fahr., and U′ the weight lost at any observed temperature, $32°+t°$, the value of U will be

$$\mathrm{U}'\{1+(w-s)t\}=\mathrm{U}'(1+0{\cdot}0001296\,t)\,;$$

and if V and V′ similarly represent the weights lost by the stirrup and end of the frame immersed,

$$\mathrm{V}=\mathrm{V}'\{1+(w-b)t\}=\mathrm{V}'(1+0{\cdot}0001209\,t).$$

Let W be the weight in air of the magnet and its appendages, then the coefficient of expansion for $t°$ above 32° expressed in parts of the force will be

$$\frac{\mathrm{U}\times 0{\cdot}0001296+\mathrm{V}\times 0{\cdot}0001209}{\mathrm{W}}\,t.$$

In the present instance the value of this coefficient is

$$0{\cdot}00001022\,t, \text{ or } 0{\cdot}00001t \text{ nearly},$$

and the value of x being diminished by this quantity, the whole temperature coefficient will be

$$0{\cdot}00050528\,t+0{\cdot}0000013555t^2.$$

The temperature coefficient of the bar (C.B. IX.) similarly determined is

$$0{\cdot}0003822\,t+0{\cdot}0000009477t^2.$$

In both these instances, it will be seen that the temperature coefficient varies considerably from the uniform law usually employed in the reduction of magnetic ob-

servations*; and as it is impossible to foresee what points of scientific interest in the investigation of magnetic changes may depend on the determination of small quantities, and on the relation of magnetic variation in warm and cold climates, it may be considered not undesirable to ascertain, with the greatest attainable degree of accuracy, the temperature coefficients of all magnets to be employed in observing the changes of force. In the method here proposed, the magnet is under circumstances precisely similar to those which would exist when it is subsequently used in observation; it may therefore be considered less open to objection than the ordinary method of deflection, by which the temperature coefficient is inferred from the mutual action of two magnets and the earth on each other. Amongst other sources of uncertainty in the latter method, may be mentioned the unexplained difference in the result that has frequently been observed, according as the marked or unmarked pole of the deflecting, has been turned towards the deflected magnet; arising probably from the unequal, and possibly variable, distribution of magnetism throughout the bar; which conditions, if they really exist, will have precisely the same effect on the indications of the magnet when under trial, as they would have when it is in actual use.

By introducing the differences only of the scale-readings into the calculation, large numerical quantities are avoided, as well as the necessity of adopting a zero point, or scale-reading corresponding to no deflecting force.

* The fact of the decrease of magnetic intensity not being in the simple ratio of the increase of temperature, but in some higher ratio, was it is believed first announced by Professor Christie, Sec. R.S., in the Philosophical Transactions, 1825, p. 63.

Keppel Street, 1849, *June* 21.

V. *Researches regarding the Molecular Constitution of the Volatile Organic Bases.*

By Dr. A. W. Hofmann, *F.C.S., Professor of the Royal College of Chemistry of London. Communicated by Sir* James Clark, *Bart., F.R.S.*

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THE limited number of elementary substances which are concerned in the elaboration of the endless variety of organic compounds, long ago directed the course of chemical inquiry into the channel of speculations as to the mode in which the various constituents are grouped in bodies of this nature. The necessity of these speculations became more and more imperative as the boundary of the science extended; they were indeed forced upon us by the discovery of substances isomeric with each other which deprived us of the resort to mere quantity for the explanation of their contrasting qualities. Wild and incongruous though some of the views, proposed from time to time, may have been, it must be admitted that their influence upon the progress of chemistry has been most beneficial; especially in the organic department of this science, it is to the theory of the compound radicals, the result of these speculations, that we are indebted for the light which now begins to dawn upon the chaos of collected facts, even if we should never succeed in isolating these radicals.

Among the various classes of organic substances, there is perhaps none of which, from an early period, chemists have so constantly endeavoured to attain a general conception as the group of compounds which have received the name of organic bases, all—and they are now very numerous—being capable of combining, like the metallic oxides, with acids, and being derived either from vital processes in animals or plants, or from a variety of artificial reactions conducted in the laboratory.

The remarkable analogy between all these substances and ammonia, which in its turn imitates as it were in its chemical deportment the mineral oxides, naturally attracted the notice of chemists soon after Sertürner's discovery of the first of these alkaloids in the beginning of this century. Nor have they ever since been classified separately from ammonia; philosophers have only differed as to the mode of their relation with the typical compound.

Of the theories which have been enunciated respecting the constitution of the organic bases, there are two of chief importance, which may be designated as the ammonia- and the amidogen-theory, the former having been first proposed by Berzelius*, while the latter we owe to Liebig†. According to the former of the two

* Traité de Chimie, vi. p. ii.

† Handwörterbuch der Chemie von Liebig, Wöhler und Poggendorff, Bd. i. p. 699. Artikel Organische Basen.

chemists, the ammonia would pre-exist in the organic bases; these bodies would be conjugated compounds of ammonia with various adjuncts, containing either carbon and hydrogen, or these elements together with nitrogen, oxygen and even sulphur, compounds in which the original character of the ammonia has only been slightly modified by the accession of the adjunct. This view is chiefly supported by the mode and the proportions in which these alkaloids combine with acids, and by the fact, that various organic substances, by directly uniting with ammonia, give rise to the formation of basic compounds which are perfectly analogous to the alkaloids occurring in the economy of nature. According to Liebig's opinion, ammonia would no longer exist in the organic bases. At the time when Liebig* wrote upon this subject, the attention of chemists was much engaged with the study of a class of compounds, known under the name of amides, the prototype of which, oxamide, was discovered by Dumas. These substances, all strictly neutral, originate from ammonia by the loss of one equivalent of hydrogen, which is abstracted by the oxygen or chlorine of certain electro-negative bodies (as in the formation of oxamide and benzamide), a hypothetical substance, amidogen, H_2N, remaining in combination with the oxide or chloride, deprived of 1 equiv. of oxygen or chlorine. Liebig thought that the formation of the organic bases might take place in a similar manner, namely, by a reduction of ammonia to the state of amidogen, by the action of electro-positive organic oxides.

Each of these theories being expressed in a simple formula, the organic bases, according to Berzelius, would be represented by the terms

$$H_3N+X,$$

while Liebig's view would characterize them as

$$H_2N+Y,$$

X denoting generally an organic compound containing carbon, hydrogen, and pos sibly nitrogen, oxygen and sulphur, while Y expresses an organic oxide, chloride, &c., *minus* 1 equiv. of oxygen, chlorine, &c.

Objections have been raised against either theory, and the opinions of chemists have remained divided. Liebig has not returned any more to the subject, but Berzelius took frequent occasion, both in his 'Annual Report' and in the several editions of his 'Traité,' to defend his notion by the skilful interpretation of every new fact which was elaborated by the progress of the science. The weight of his authority has not been without influence, for it cannot be denied that Berzelius's view has become more and more generally accepted, especially since a series of comparative researches, conducted of late upon the derivatives of the salts of ammonia and of organic bases, appeared to give fresh support to this theory. These experiments pointed out that the elimination of hydrogen from organic bases and ammonia is by no means confined to one equivalent; oxalate of ammonia, which by the loss of 2 equivs. of water is converted into oxamide, when deprived of the whole of its hydrogen in

* *Loc. cit.* p. 235.

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the form of water, becomes cyanogen (oxalonitrile); an analogous change occurs with the acid salts of ammonia, resulting in the formation of two classes of compounds, differing, the one by two, the other by four equivalents of water, from the original salt.

The representation of several of these groups in analogous derivatives from the salts of organic bases, especially from the salts of aniline, could not but strengthen the belief that ammonia actually pre-exists in the organic alkaloids. Incidentally to some researches communicated to the Chemical Society of London*, I gave a synopsis of all the facts supporting the view of BERZELIUS.

The prosecution however of this inquiry has elicited many points, which are scarcely reconcileable with this theory. In another paper† I endeavoured to show that the force of the argument in favour of this view, derived from the considerations just stated, is greatly neutralized on the completion of the comparison between the two series by the failure of the analogy, just at the point where its occurrence would have been most decisive. Now this very failure is not only in perfect harmony with, but would be required by, the theory of amidogen-bases.

Yet stronger grounds for the acceptation of the latter view have been afforded by a splendid investigation of M. WURTZ‡ on the compounds of ethers with cyanic acid, which have actually realized a series of substances, anticipated in a most remarkable manner by LIEBIG on the theoretical ground of his conception of the nature of these compounds. Instances of such anticipation of discovery are so rare, that I may be allowed to quote the words in which LIEBIG predicted nearly ten years ago the discovery of M. WURTZ:—"If," said LIEBIG §, in continuing the development of his ideas respecting the constitution of the organic bases, "we were enabled to replace by amidogen the oxygen in the oxides of methyl and ethyl, in the oxides of two basic radicals, we should without the slightest doubt obtain a series of compounds exhibiting a deportment similar in every respect to that of ammonia. Expressed in symbols, a compound of the formula

$$C_4 H_5, H_2 N = E, Ad$$

would be endowed with basic properties."

Now these compounds, imagined in 1840 by LIEBIG in illustration of his views, have sprung into existence in 1849, with all the properties assigned to them by that chemist. At the beginning of the present year, M. WURTZ, in investigating the cyanates of ethyl, methyl and amyl, arrived at the unexpected result that these compounds, when decomposed by potassa, undergo a change analogous to that of cyanic acid. This acid, when treated with potassa, yielding carbonic acid and ammonia, the corresponding ethers were split into carbonic acid and compound ammonias of the exact formula indicated in LIEBIG's suggestion.

It would be difficult to imagine a more brilliant triumph for any theoretical specu-

* Researches on the Volatile Organic Bases, III. Action of Chloride, Bromide and Iodide of Cyanogen upon Aniline, Chem. Soc. Quart. Journ. i. p. 285.

† Chem. Soc. Quart. Journ. ii. p. 331. ‡ Compt. Rend. xxviii. p. 223. § *Loc. cit.* p. 235.

lation; I have however no doubt that even the illustrious propounder of this view is at present far from believing that all the organic bases are amidogen-compounds. The progress of our knowledge has changed the form of this view, without shaking its foundation. A good theory is more than a *temporary* expression of the state of science, collecting under a general view the facts acquired up to the moment of its birth. It will not, like ephemeral hypothesis, vanish before the light of succeeding discoveries, but expanding with the growth of science, it will still correctly represent the known facts, though of necessity modified into a more general expression.

Such a theory then was that of Liebig. Resting as it did, upon the facts observed in the formation of the neutral amides, it was, as originally framed, an expression of the knowledge we then possessed. Subsequent researches showed that it was not only the 1 equiv. of hydrogen (the abstraction and replacement of which had led us to amidogen and the amides) that could be removed from the ammonia, but that similarly 2 equivs., and even the whole of the hydrogen could be withdrawn from their position in this base and substituted by other atoms, as in the imides and nitriles.

If then we give to Liebig's view the extension of which it naturally admits, and which is demanded by the onward steps of science, we arrive at a more general conception of the nature of the organic bases; amidogen and the amides now presenting themselves to us only as particular instances of the permutations possible among the elements of the primary type ammonia. It seemed but logical to look among the bases for analogues too of the imidogen-compounds and the nitriles. In other words, it appeared desirable to inquire whether the several equivalents of hydrogen in ammonia could not be replaced, not only by atoms neutralizing the basic properties of the original system, but also by elements or groups of elements, not affecting, or but slightly modifying the alkaline character of the primary compound. Were this possible, we should arrive at the formation of three classes of organic bases, derived from ammonia by the replacement respectively of 1, 2 or 3 equivalents of hydrogen.

Expressed in formulæ, these compounds would be—

$$\left.\begin{matrix} H \\ H \\ H \end{matrix}\right\} N = \text{Ammonia.}$$

$$\left.\begin{matrix} H \\ H \\ X \end{matrix}\right\} N = \text{Bases of the first class, provisionally called amidogen-bases.}$$

$$\left.\begin{matrix} H \\ X \\ Y \end{matrix}\right\} N = \text{Bases of the second class, provisionally called imidogen-bases.}$$

$$\left.\begin{matrix} X \\ Y \\ Z \end{matrix}\right\} N = \text{Bases of the third class, provisionally called nitrile-bases.}$$

The bases belonging to the first class are pretty numerously represented. Aniline, methylamine, ethylamine, amylamine, when considered as amidogen-compounds, belong to this group.

$$\left.\begin{matrix} H \\ H \\ C_{12}H_5 \end{matrix}\right\} N = \text{Aniline} \qquad \left.\begin{matrix} H \\ H \\ C_2H_3 \end{matrix}\right\} N = \text{Methylamine} \qquad \left.\begin{matrix} H \\ H \\ C_4H_5 \end{matrix}\right\} N = \text{Ethylamine} \qquad \left.\begin{matrix} H \\ H \\ C_{10}H_{11} \end{matrix}\right\} N = \text{Amylamine.}$$

Bases of the second and third of the above classes had not been hitherto obtained, although it is not improbable that many of the alkaloids, whose constitution is at present perfectly unknown, may be found on a closer investigation to be members of these latter groups.

The researches which I have the honour of presenting to the Royal Society will exhibit a series of artificial bases, which are evidently produced, by the substitution of carbohydrides, for the second and third equivalents of hydrogen in the ammonia.

Before proceeding however to the details of my experiments, I shall state, that I am far from supposing that the above formulæ include the constitution of all the complex bases with which we are acquainted. It is chiefly the volatile alkaloids whose constitution may be represented by this view, but even here exceptions may occur.

Both the ammonia- and the amidogen-theory of the organic bases appear to me to have the same defect, in that they endeavour to compress into a single proposition our notions respecting the endless variety of compounds which are united under the collective term organic bases. If we reflect upon the manifold sources from which the various groups of alkaloids are derived and the differences which we observe in their physical properties, and even in their chemical deportment, it is but natural to assume that in their constitution a diversity may exist similar to that of the organic acids, which we cannot attempt to include under one common theory of construction. On comparing the alkaloids of the Cinchona bark with urea and creatinine, or with nicotine and aniline, few chemists indeed will be inclined to believe that the constituents in these various substances are arranged in the same manner. The constitution of the non-volatile organic bases will probably present a very considerable diversity; and it is not at all unlikely that this class will exhibit even instances of conjugated ammonias in Berzelius's acceptation of the term.

In commencing my experimental inquiry, the first step was to select the particular base which should be the subject of operation, and the radicals whose introduction should be attempted. On the one hand, my previous experimental occupations suggested aniline for the foundation; while, on the other, the radicals existing in aniline and its congeners, methylamine, ethylamine and amylamine, namely, phenyl, methyl, ethyl and amyl, presented themselves as materials for construction.

Action of Phenyl-alcohol on Aniline.

My endeavours to introduce into aniline a second equivalent of phenyl, in order to convert

$$\left.\begin{matrix} H \\ H \\ C_{12}H_5 \end{matrix}\right\}N \quad \text{into} \quad \left.\begin{matrix} H \\ C_{12}H_5 \\ C_{12}H_5 \end{matrix}\right\}N$$

have been unsuccessful up to the present moment. I had hoped that this conversion might be effected by the action of phenyl-alcohol on aniline according to the following equation:—

$$\left.\begin{matrix} H \\ H \\ C_{12}H_5 \end{matrix}\right\}N + H\,O, C_{12}H_5\,O, = \left\{\begin{matrix} H \\ C_{12}H_5 \\ C_{12}H_5 \end{matrix}\right\}N + 2H\,O.$$

Phenyl-alcohol, however, has neither at the common nor at a high temperature—the mixture was exposed for several days in a sealed tube to 250° in an oil-bath—any action upon aniline. The residuary aniline was identified by analysis. When converted into a platinum-salt—

0·3120 grm. of the salt left on ignition 0·1024 grm. of platinum.

Experimental percentage of platinum.	Theoretical percentage in the aniline-platinum-salt.
32·82	32·98

This experiment, when repeated for a longer period, might possibly give a more satisfactory result. It is known that ammonia, by a similar treatment with phenyl-alcohol, is likewise only very slowly converted into aniline.

The action of chloride and bromide of phenyl $C_{12}H_5Cl$, and $C_{12}H_5Br$ upon aniline promised a better result; but the difficulties which I encountered in preparing these compounds, which are as yet but very imperfectly investigated, deterred me from farther pursuing this direction of the inquiry.

Much more successful were my endeavours to substitute methyl, ethyl and amyl for the remainder of the basic hydrogen in aniline. The compounds of these radicals with chlorine, bromine and iodine appeared to be the most appropriate substances for this purpose. I have worked with these three classes of compounds, but finding that the use of the chlorides and iodides is attended with inconveniences, the former compounds being exceedingly difficult to handle on account of their volatility, while the latter often complicate the reactions by the rapid decomposition of the hydriodic acid formed in the process, I have almost exclusively employed the bromides, whose action is so precise and definite as to preclude the necessity of seeking any farther agent; only when working in the methyl-series I have sometimes preferred to employ the iodide, which is far less volatile than the bromide. Still the deportment of the iodides presents some peculiarities, which require farther elucidation.

Action of Bromide of Ethyl upon Aniline.

On adding dry bromide of ethyl to aniline, no change takes place in the cold, but on gently heating the mixture in an apparatus which will allow the volatilized bromide to return to the aniline, a lively reaction ensues. The liquid remains for some time in a state of ebullition, and solidifies on cooling into a mass of crystals. If a

cold mixture of the two bodies be left for a few hours, it deposits crystals, which are much more definite than those obtained on the cooling of the hot solution. In either case the fluid assumes a deep amber colour which approaches brown, and the crystals are usually slightly yellow. These crystals vary in composition according to the proportions in which the two bodies have been mixed. If a very large excess of aniline has been used, they are of a prismatic character, and consist of pure hydrobromate of aniline. This compound was identified by analysis:—

0·0486 grm. of the crystals gave 0·0525 grm. of bromide of silver.

Experimental percentage of bromine.	Theoretical percentage of bromine in hydrobromate of aniline.
45·88	45·97

On the other hand, if the bromide of ethyl predominates to a considerable extent, the crystals are flat, four-sided tables, sometimes of considerable size. Several analyses, the details of which will be found below, showed that they were the hydrobromate of a new base*, represented by the formula—

$$C_{16}H_{11}N = C_{12}\left\{\begin{matrix} H_6 \\ C_4H_5 \end{matrix}\right\}N = \left\{\begin{matrix} H \\ C_{12}H_5 \\ C_4H_5 \end{matrix}\right\}N,$$

i. e. of aniline in which 1 equiv. of hydrogen is replaced by 1 equiv. of ethyl, or ammonia in which 2 equivs. of hydrogen are replaced, the one by phenyl, the other by ethyl. The same base is contained in the free state, either alone or mixed with aniline in the mother-liquor of the crystals of hydrobromate of aniline, while the mother-liquor of the hydrobromate of the new base, especially if a large excess of the bromide has been employed, and after some days' standing, consists of nearly perfectly pure bromide of ethyl, only a small quantity of the hydrobromate in question being kept in solution.

The formation of the new basic compound, for which I propose the name Ethylaniline or Ethylophenylamine, takes place by the removal, from aniline, of 1 equiv. of hydrogen, in the form of hydrobromic acid, for which an equivalent of ethyl is substituted, the compound thus produced uniting with the hydrobromic acid. Hence the action of bromide of ethyl upon aniline may be represented by the following two simple equations:—

$$\underbrace{2\,C_{12}H_7N}_{\text{Aniline.}} + \underbrace{C_4H_5Br}_{\text{Bromide of Ethyl.}} = \underbrace{C_{12}H_7N,HBr}_{\text{Hydrobromate of Aniline.}} + \underbrace{C_{16}H_{11}N}_{\text{Ethylaniline.}}$$

$$\underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{C_4H_5Br}_{\text{Bromide of Ethyl.}} = \underbrace{C_{16}H_{11}N,HBr}_{\text{Hydrobromate of Ethylaniline.}}$$

* Frequently, as may be imagined, mixtures of the two hydrobromates are deposited according to the proportion in which the constituents are mixed.

Ethylaniline (*Ethylophenylamine*).

This base may be readily obtained in a state of purity by decomposing the solution of the hydrobromate with a concentrated solution of potassa. A brown basic oil rises at once to the top of the liquid; it is separated by means of a pipette or a tap-funnel, and subjected to rectification, after having been freed from water by standing over solid potassa. Thus a colourless transparent oil is obtained, which rapidly turns brown on exposure to air and light, and has a very high refractive power. It has all the properties of the oily bases in general. From aniline it is distinguished by a slight difference in the odour, perhaps imperceptible to an inexperienced nose, by a higher boiling-point and a lower specific gravity. Ethylaniline boils (from platinum) constantly at 204°, the boiling-point of aniline being 182°; the specific gravity of this base is 0·954 at 18°, that of aniline being 1·020 at 16°. Ethylaniline does not exhibit the violet coloration with chloride of lime which characterizes aniline. Its acid solutions impart a yellow colour to fir-wood and the pith of elder-tree, although less intensely than those of aniline. By dry chromic acid the base is inflamed like aniline.

Analyses performed with protoxide of copper gave the following results:—

I. 0·2566 grm. of oil gave 0·7470 grm. of carbonic acid*.

II. 0·3048 grm. of oil gave 0·8850 grm. of carbonic acid, and 0·2544 grm. of water.

	Percentage-composition.	
	I.	II.
Carbon	79·39	79·19
Hydrogen . . .	——	9·27

The formula

$$C_{16} H_{11} N$$

requires the following values:—

	Theory.		Mean of experiments.
16 equivs. of Carbon	96	79·33	79·28
11 equivs. of Hydrogen	11	9·09	9·27
1 equiv. of Nitrogen	14	11·58	——
1 equiv. of Ethylaniline	121	100·00	

The salts of ethylaniline are remarkable for their solubility, especially in water. They are not easily obtained in well-defined crystals from an aqueous solution. From alcohol, in which they are somewhat less soluble than in water, several salts may be readily crystallized. Both the hydrochlorate and oxalate are obtained only on evaporating their solutions nearly to dryness, when the salts separate in the form of radiated masses; the sulphate and nitrate have not as yet been obtained in the solid form.

* The hydrogen was lost.

Hydrobromate of Ethylaniline.

The hydrobromate is extremely soluble in water, but crystallizes on spontaneous evaporation of its alcoholic solution in splendid regularly formed tables, of considerable size and perfect beauty. I intend to give the measurement of these crystals in a future communication. The analyses of this salt, dried at 100°, gave the following results:—

I. 0·6412 grm. of hydrobromate gave 0·5956 grm. of bromide of silver.
II. 0·5553 grm. of hydrobromate gave 0·5216 grm. of bromide of silver.

Percentage of Hydrobromic Acid.	
I.	II.
40·01	40·47

The formula

$$C_{16}H_{11}N, HBr$$

requires the following values:—

	Theory.		Mean of experiment.
1 equiv. of Ethylaniline	121	59·91	——
1 equiv. of Hydrobromic Acid	81	40·09	40·24
1 equiv. of Hydrobromate of Ethylaniline	202	100·00	

The hydrobromate of ethylaniline when gently heated sublimes, like the corresponding aniline-salt, in splendid needles, but when subjected to the action of a rapidly increasing heat it undergoes a very remarkable decomposition, being redecomposed into aniline and bromide of ethyl. On addition of hydrochloric acid to the distillate, the aniline dissolves, while the bromide of ethyl collects as a heavy oil at the bottom of the vessel.

$$\underbrace{C_{16}H_{11}N, HBr}_{\text{Hydrobromate of Ethylaniline.}} = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{C_4H_5Br}_{\text{Bromide of Ethyl.}}$$

I have in vain tried to split hydrobromate of aniline according to the equation

$$\underbrace{C_{12}H_7N, HBr}_{\text{Hydrobromate of Aniline.}} = H_3N + \underbrace{C_{12}H_5Br}_{\text{Bromide of Phenyl.}}$$

This salt sublimes, even when suddenly heated, without any decomposition.

Platinum-Salt of Ethylaniline.

I have controled the formula of ethylaniline moreover by the analysis of the platinum double salt of this substance. This salt is likewise very soluble, and may by this property be distinguished from the corresponding aniline-salt; on addition of a concentrated solution of bichloride of platinum to a concentrated solution of this

hydrochlorate, a deep orange-red oil is deposited, which solidifies, sometimes only after half a day, with crystalline texture. If a moderately concentrated solution be employed, the salt crystallizes in the course of a few hours in magnificent yellow needles, often of an inch in length. On account of its great solubility in water and alcohol, it has to be washed with a mixture of alcohol and ether, in which the latter predominates. It may be dried at 100° without decomposition.

On analysis the following numbers were obtained:—

0·3550 grm. of platinum-salt gave 0·3275 grm. of carbonic acid and 0·1055 grm. of water.

0·1812 grm. of platinum-salt gave 0·0545 grm. of platinum.

The formula

$$C_{16}H_{11}N, H Cl, Pt Cl_2$$

requires the following values:—

	Theory.		Experiment.
16 equivs. of Carbon	96·00	29·34	29·24
12 equivs. of Hydrogen	12·00	3·66	3·83
1 equiv. of Nitrogen	14·00	4·29	——
3 equivs. of Chlorine	106·50	32·55	——
1 equiv. of Platinum	98·68	30·16	30·07
1 equiv. of Platinum-salt	326·18	100·00	

Terchloride of gold and protochloride of mercury yield with solutions of ethylaniline yellow oily precipitates, which are very readily decomposed.

Of the products of decomposition of ethylaniline, I know as yet almost nothing, although they will not be deficient in interest in a theoretical point of view.

The action of bromine gives rise to the formation of two compounds, both crystalline, one basic, the other indifferent and corresponding probably to tribromaniline. Neither of these substances has yet been analysed.

On passing cyanogen into an alcoholic solution of ethylaniline, short yellow prisms are deposited after some time, which are evidently cyanethylaniline, Cy, $C_{16}H_{11}N$, corresponding to cyaniline and cyanocumidine*. This new cyanogen-base dissolves in dilute sulphuric acid, and is thrown down from this solution by ammonia in form of a floury precipitate. The hydrochlorate, like the corresponding cyaniline-salt, is very insoluble in hydrochloric acid. It may be obtained in fine crystals on addition of hydrochloric acid to a solution of the base in dilute sulphuric acid. Cyanethylaniline, like cyaniline, forms a very soluble platinum-salt.

I have made also some qualitative experiments respecting the deportment of ethylaniline with chloride of cyanogen. This gas is rapidly absorbed, much heat being evolved. On cooling, the mass solidifies into a resinous mixture of a hydrochlorate and a neutral oil, which separates on addition of water. The base separated from

* Chemical Society, Quart. Journ. i. p. 159.

the hydrochlorate is an oil, and volatile, while melaniline, produced in the corresponding reaction of chloride of cyanogen with aniline, is solid and non-volatile.

Bisulphide of carbon gives rise to a gradual evolution of hydrosulphuric acid, no crystals being deposited from the mixture.

Phosgene gas acts powerfully on ethylaniline, a liquid compound being formed together with hydrochlorate of ethylaniline. No analysis having as yet been performed of these compounds, I refrain from entering into any farther details.

Action of Bromide of Ethyl upon Ethylaniline.

The phenomena attending the action of bromide of ethyl upon ethylaniline resemble those which are observed in the corresponding treatment of aniline. The reaction however is less powerful, another equivalent of hydrogen in aniline being less easily eliminated or replaced. Four or five days elapse before the separation of crystals commences at the common temperatures. The formation however is considerably accelerated on application of heat.

The experience obtained in the preparation of ethylaniline suggested at once the use of a very large excess of bromide of ethyl, by which the formation of one compound only was secured. The mixture assumed a light-yellow colour, turned gradually brown, and deposited after five days four-sided tables of considerable size and remarkable beauty. The mother-liquor was coloured bromide of ethyl, leaving, when distilled off, a small quantity of the same crystalline compound.

The substance in question was, as a subsequent analysis will prove, the pure hydrobromate of a new base, which is represented by the formula—

$$C_{20}H_{15}N=C_{16}\left\{\begin{matrix}H_{10}\\C_4H_5\end{matrix}\right\}N=C_{12}\left\{\begin{matrix}H_5\\C_4H_5\\C_4H_5\end{matrix}\right\}N=\left\{\begin{matrix}C_{12}H_5\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}N,$$

i. e. of ethylaniline in which 1 equiv. of hydrogen is replaced by ethyl, or aniline in which 2 equivs. of the same radical are substituted for a corresponding number of hydrogen-equivalents, or lastly ammonia, in which the three equivalents of hydrogen are replaced, the one by phenyl, the two others each by ethyl.

The formation of this new substance, for which I propose the name diethylaniline or diethylophenylamine, requires no farther illustration: it is absolutely analogous to the production of ethylaniline.

Diethylaniline (*Diethylophenylamine*).

The preparation of this compound in a state of purity resembles that of the preceding base, whose physical properties have been only slightly modified by the introduction of the second equivalent of ethyl. The specific gravity was found to be 0·939 at 18°, showing a slight decrease when compared with that of ethylaniline (0·954). The boiling-point, however, was raised nearly 10 degrees; diethylaniline boils quite constantly at 213°·5. Diethylaniline is moreover distinguished from ethylaniline by re-

maining perfectly bright and colourless when exposed to the air. Like ethylaniline it still imparts a yellow colour to fir-wood, but, like the former, fails to affect a solution of hypochlorite of lime.

Analysis performed with protoxide of copper gave the following results:—

0·2301 grm. of oil gave 0·6814 grm. of carbonic acid and 0·2118 grm. of water.

The formula

$$C_{20}\,H_{15}\,N$$

requires the following values, which may be placed in juxtaposition with the percentage deduced from the above analysis.

	Theory.		Experiment.
20 equivs. of Carbon	120	80·53	80·76
15 equivs. of Hydrogen . . .	15	10·06	10·22
1 equiv. of Nitrogen	14	9·41	——
1 equiv. of Diethylaniline . .	149	100·00	

To obtain farther evidence for the formula of this compound, both the hydrobromate and the platinum-salt were subjected to analysis.

Hydrobromate of Diethylaniline.

I have mentioned this salt when speaking of the formation of the second base. It is extremely soluble, and resembles in every respect the corresponding ethylaniline-compound. The bromine-determination gave the following results:—

0·4277 grm. of salt gave 0·3490 grm. of bromide of silver.

I place the experimental percentage of hydrobromic acid in juxtaposition with the theoretical value of the formula

$$C_{20}\,H_{15}\,N,\,H\,Br.$$

	Theory.		Experiment.
1 equiv. of Diethylaniline	149	64·78	——
1 equiv. of Hydrobromic acid	81	35·22	35·14
1 equiv. of Hydrobromate of Diethylaniline	230	100·00	

The hydrobromate of diethylaniline, when gently heated, fuses and sublimes like the corresponding aniline- and ethylaniline-salts. When rapidly heated, it is entirely converted into a colourless oil, which distils over. This oil contains equal equivalents of bromide of ethyl and ethylaniline. By this distillation we obtain indeed the very constituents from which the hydrobromate was originally prepared, and which would of course reconvert themselves into hydrobromate of diethylaniline. Only a trifling amount of undecomposed hydrobromate covers, after the distillation is finished, the sides of the retort in the form of a radiated coating.

The peculiar deportment then of the hydrobromates of the ethyl-bases, and probably of all their salts, allows us to remove the several equivalents of ethyl one after

the other from our fabric in the same manner as we had inserted them. When first I became acquainted with diethylated aniline, having then already observed the deportment of the salts of ethylaniline, which under the influence of heat are reconverted into aniline, I indulged for a moment in the pardonable illusion, that the salt of diethylaniline would exhibit the metamorphosis—

$$\underbrace{C_{20}H_{15}N, HBr}_{\text{Hydrobromate of Diethylaniline.}} = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{C_8H_9Br}_{\text{Bromide of Butyl.}}$$

a mode of reaction which would have afforded a passage from the ethyl- into the butyl-series. This step however is reserved for a more fortunate experimenter.

Platinum-salt of Diethylaniline.

This salt resembles the corresponding compound of ethylaniline. On addition of a concentrated solution of bichloride of platinum to the hydrochlorate, it is precipitated in form of a deep orange-coloured oil, which rapidly solidifies into a hard crystalline mass. If the solutions are mixed in a dilute state, the salt is separated after some time in cross-like yellow crystals. It is not nearly so soluble in water and alcohol as the ethylaniline-salt. Analysis led to the following numbers :—

*I. 0·1715 grm. of platinum-salt gave 0·2125 grm. of carbonic acid and 0·0700 grm. of water.

*II. 0·1848 grm. of platinum-salt gave 0·0513 grm. of platinum.

III. 0·5361 grm. of platinum salt gave 0·1476 grm. of platinum.

IV. 0·5550 grm. of platinum-salt gave 0·1533 grm. of platinum.

	Percentage-composition.			
	I.	II.	III.	IV.
Carbon	33·78	——	——	——
Hydrogen	4·53	——	——	——
Platinum	——	27·76	27·53	27·62

The formula

$$C_{20}H_{15}N, HCl, PtCl_2$$

requires the following values, which I place in juxtaposition with the mean of the experimental results :—

	Theory.		Mean of experiments.
20 equivs. of Carbon	120·00	33·78	33·78
16 equivs. of Hydrogen	16·00	4·54	4·53
1 equiv. of Nitrogen	14·00	3·91	——
3 equivs. of Chlorine	106·50	29·99	——
1 equiv. of Platinum	98·68	27·78	27·66
1 equiv. of Platinum-salt	355·18	100·00	

* I. and II. are of a specimen recrystallized from alcohol.

I have not examined any other of the salts of diethylaniline: their deportment resembles in every respect that of the ethylaniline-salts.

Action of Bromide of Ethyl on Diethylaniline.

If we assume that the series of bases, aniline, ethylaniline and diethylaniline, arise from the gradual elimination of the three equivalents of hydrogen in ammonia, and their substitution by 1 equivalent of phenyl and 2 equivalents of ethyl, it is difficult to imagine that bromide of ethyl should have any farther action on diethylaniline, this compound ammonia containing, according to this view, no longer any replaceable hydrogen. However, it would have been deserting the path of inductive research, if this point had been left unestablished by rigorous experiments.

For this purpose diethylaniline was left in contact with bromide of ethyl for nearly a month. After the lapse of this time the mixture had undergone no change in its appearance. On treating however a portion with water, it was found that a small quantity of hydrobromate dissolved, from which on addition of potassa an oily base was separated. The quantity obtained in this manner from nearly two ounces of the united liquids being insufficient for a determination, I subjected a similar mixture, in a sealed tube, for several days to the temperature of boiling water. I was surprised to find that a yellow layer began to separate at the lower extremity of the tube, which increased gradually to a fifth of the liquid column. When allowed to cool, this layer solidified into a crystalline mass. On opening the tube, it was found that there was no pressure from within, except that exerted by the elasticity of bromide of ethyl. After separation of the excess of the bromide by distillation in the water-bath, water added to the viscid residue dissolved the crystals, while an oil floated upon the surface which was found to be entirely basic: it was separated by a distillation at a higher temperature, when it was carried over with the vapour of the water. The remaining liquid in the retort was found to be a solution of a hydrobromate. It was decomposed with potassa, and the liberated base separated from the bromide of potassium by distillation. The two basic oils obtained in this manner, when dissolved in hydrochloric acid and precipitated by bichloride of platinum, gave rise to the formation of two splendid platinum-salts. These salts left on ignition the following percentage of platinum; I. being the oil which had not been in combination; II. the base which had been separated from the hydrobromate.

I. 0·5626 grm. of platinum-salt left 0·1559 grm. of platinum.

II. 0·5384 grm. of platinum-salt left 0·1495 grm. of platinum.

Experimental percentage of platinum.		Theoretical percentage in diethylaniline-platinum-salt.
I.	II.	
27·70	27·76	27·78.

These experiments prove that the basic oil obtained on direct distillation, or by distilling after treatment with potassa, had not assimilated a farther equivalent of

the alcohol-radical; but the question arose in what manner a portion of the base had been converted into hydrobromate? It was not impossible that the bromide of ethyl, although it had been in contact with chloride of calcium, might nevertheless still have retained a portion of water, whose elements could have induced a regeneration of alcohol with simultaneous formation of hydrobromic acid:

$$\underbrace{C_4\,H_5\,Br}_{\text{Bromide of Ethyl.}}+2H\,O=\underbrace{H\,O,\,C_4\,H_5\,O}_{\text{Alcohol.}}+H\,Br.$$

I now took care that both substances, the diethylaniline and the bromide of ethyl, should be perfectly dry before coming into contact. For this purpose, both liquids were left for several days over anhydrous caustic baryta and then subjected to distillation. The compounds at the common temperature were found to have no action upon one another. In order to place them in a condition most favourable for mutual action, the mixture was exposed for several days in a sealed tube to the temperature of boiling water. On opening the tube and extracting the mixture with water, a small quantity of hydrobromate was found to have nevertheless been formed. The portion insoluble in water was dissolved in hydrochloric acid and precipitated by bichloride of platinum. The salt obtained in this manner could not be mistaken. It fell down in the form of a yellow oil, which rapidly solidified into the orange-yellow crystalline aggregates characterizing the diethylaniline-compound.

From these experiments, it would appear that diethylaniline is no longer capable of fixing another equivalent of ethyl. Still the production of the small quantity of hydrobromate in the *last* experiment indicates that the phenomenon cannot be due to the formation of alcohol. Farther steps are necessary for the explanation of this transformation.

In aniline, ethylaniline and diethylaniline, then we have three bases, which may be considered as derived from ammonia by the elimination and replacement of its three hydrogen-equivalents. The successive formations of ethylaniline and diethylaniline from aniline have been detailed in the preceding paragraphs; the passage of ammonia into aniline, when exposed to the action of a phenyl-compound, has been proved at an earlier period by some experiments, made jointly by M. Laurent and myself, upon the action, at a high temperature, of hydrated oxide of phenyl on ammonia. In this reaction a small but unequivocal quantity of aniline is formed.

The formation of aniline, ethylaniline and diethylaniline, appeared to have established in a sufficiently satisfactory manner, the point of theory which is here in question; still I thought desirable the acquisition of additional facts in support of the position to which this inquiry has conducted me. Thus I have been led to study the action of bromide of ethyl upon several of the derivatives of aniline, and to try whether other alcohol-radicals, such as methyl and amyl, would have a similar

action; lastly, in order to complete the investigation, I was obliged to leave the amidogen-bases altogether in order to submit the typical ammonia itself to examination.

Among the bases derived from aniline, there is a class whose deportment with bromide of ethyl appeared to be more particularly worthy of a careful investigation. This is the group of compounds produced from aniline by substitution, and embracing chloraniline, dichloraniline and trichloraniline, the corresponding bromanilines, iodaniline and nitraniline. The question arose in what manner will these substances, in which the original aniline has lost already a certain quantity of its hydrogen, comport themselves under the influence of bromide of ethyl? The answer afforded by experiment was unequivocal and in perfect accordance with the result anticipated by theory, although it may here at once be stated, that the difficulty of obtaining the compounds in question in sufficient quantity has prevented me from pursuing this part of the investigation as far as I could have wished.

Action of Bromide of Ethyl upon Chloraniline.

A solution of chloraniline in dry bromide of ethyl exhibits no apparent change even after several days' exposure to the temperature of boiling water. On adding however water and distilling off the excess of bromide of ethyl, it was found that the chloraniline had been converted into a hydrobromate, which was held in solution, scarcely a trace of uncombined base being left. Addition of potassa to the solution of the hydrobromate separated at once a yellow oily base, of a very characteristic aniseed-odour, differing from chloraniline in many respects. It remained liquid even at the temperature of a cold winter day, while chloraniline is distinguished by the facility with which it crystallizes. Its salts are much more soluble than the corresponding chloraniline-salts: I have only seen the sulphate and oxalate in a crystallized state. This liquid base is evidently ethylochloraniline—

$$C_{16}\left\{\begin{matrix}H_{10}\\Cl\end{matrix}\right\}N.$$

I am sorry that I have not been able to verify this formula by direct analysis. The amount of substance at my disposal precluded the idea of submitting it to the processes of purification necessary before combustion. I had hoped to fix its composition by the determination of the platinum in the platinum-salt. Unfortunately this salt separated in the form of a yellow oil, which could not by any means be made to crystallize. Obliged to desist from direct analysis, I endeavoured to gain the requisite data by another mode of proceeding.

Action of Bromide of Ethyl upon Ethylochloraniline.

Recollecting that in almost all the instances which I have examined, the tendency exhibited by the various bases of producing readily crystallizable platinum-salts increased with the degree of their ethylation, I subjected the whole amount of the

still hypothetical ethylochloraniline, after having dried it by a current of hot air, to the action of a considerable excess of bromide of ethyl. After two days' exposure to 100° the mixture was found to contain a hydrobromate in solution, not a trace of free base being left. There was no doubt that a second equivalent of ethyl had been assimilated. On decomposing the hydrobromate with potassa, an oil separated resembling, in its appearance and also in its odour, the preceding compound. An attempt to purify the ethylochloraniline from the potassa by distillation with water having failed, on account of the high boiling-point of this substance, the purification of the diethylochloraniline, for as such the new compound was to be considered, was at once effected with ether. The ethereal solution of the oil was carefully washed with water to remove adhering potassa, and evaporated: the yellow oil remaining after this treatment was dissolved in hydrochloric acid, and the solution mixed with bichloride of platinum. Immediately a splendid orange-yellow crystalline precipitate was separated, which after washing with water was fit for analysis. This salt fused at 100°.

In the analysis a small quantity of platinum was lost.

0·2376 grm. of platinum-salt gave 0·0583 grm. of platinum.

The formula

$$C_{20}\,H_{14}\,Cl\,N,\,H\,Cl,\,Pt\,Cl_2,$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Diethylochloraniline .	183·50	47·09	——
1 equiv. of Hydrochloric acid . .	36·50	9·37	——
2 equivs. of Chlorine	71·00	18·22	——
1 equiv. of Platinum	98·68	25·32	24·53
1 equiv. of Platinum-salt . . .	389·68	100·00	

The result, although somewhat below theory, shows that chloraniline, when subjected to the action of bromide of ethyl, exhibits absolutely the same deportment as aniline itself, two equivalents of ethyl being consecutively introduced which give rise to the formation of two new terms, which demand the names ethylochloraniline (ethylochlorophenylamine) and diethylochloraniline (diethylochlorophenylamine).

Action of Bromide of Ethyl upon Bromaniline.

The absolute analogy existing between chloraniline and bromaniline, to which I have alluded in a former paper*, is maintained also in the deportment of these two substances towards bromide of ethyl. Bromaniline is rapidly converted into hydrobromate of ethylobromaniline which could not, except by analysis, be distinguished from the corresponding chlorine-base. The platinum-salt being likewise a viscid oil,

* Chem. Soc. Mem. ii. 291.

I have omitted to analyse it. There is however no doubt about the existence of an ethylobromaniline,

$$C_{16}\,H_{10}\,Br\,N.$$

I have not attempted to ethylate this compound any farther.

Action of Bromide of Ethyl upon Nitraniline.

Ethylonitraniline (*Ethylonitrophenylamine*).

Nitraniline readily dissolves in bromide of ethyl. The solution soon deposits, even at the common temperature, pale-yellow crystals of considerable size. At the boiling temperature of water the conversion is rapidly accomplished. On addition of an alkali to the hydrobromate, the ethylonitraniline separates as a brown oily mass, which solidifies after some time with crystalline structure. In this substance, as well as in the other ethylated bases, the properties of the mother-compound are only slightly modified. Thus we find in the base ethylonitraniline still the yellow colour of nitraniline, which it readily imparts to the skin, but which it loses altogether in its salts. These salts are as easily soluble in water as the corresponding nitraniline-compounds, if not even more so, and possess the same peculiar sweetish taste; they all crystallize however on evaporating their solutions nearly to dryness. Ethylonitraniline dissolves readily in ether and alcohol, less so in boiling water; from a solution in the latter the base is deposited in stellated groups of yellow crystals, which are readily distinguished from the felted mass of long needles, separated on cooling from an aqueous solution of nitraniline.

I have fixed the composition of ethylonitraniline by a single number, namely, by the determination of the metal in the platinum double salt. This compound is prepared by adding bichloride of platinum to a very concentrated solution of the hydrochlorate; this must not contain much free acid, in which the salt would redissolve. After a short time pale-yellow scales are separated, which have to be washed with cold water. The small quantity of substance at my disposal may excuse the slight deficiency in the amount of platinum.

0·1544 grm. of ethylonitraniline gave 0·0405 grm. of platinum.

This percentage agrees with the formula

$$C_{16}\,H_{10}\,N_2\,O_4,\,H\,Cl,\,Pt\,Cl_2,$$

as will be seen from the following comparison:—

	Theory.		Experiment.
1 equiv. of Ethylonitraniline .	166·00	44·60	——
1 equiv. of Hydrochloric acid	36·50	9·80	——
2 equivs. of Chlorine . . .	71·00	19·09	——
1 equiv. of Platinum . . .	98·68	26·51	26·23
1 equiv. of Platinum-salt . .	372·18	100·00	

The nitraniline-salt contains 28·66 per cent of platinum. I have not prepared a diethylonitraniline.

The deportment of chloraniline, bromaniline and nitraniline with bromide of ethyl, appears to throw much light upon the constitution of these substitution-bases. The possibility of introducing into these substances two equivalents of ethyl, shows that they must contain the same amount of basic hydrogen (an expression by which I may be allowed to represent briefly the hydrogen of the ammonia-skeleton) as aniline itself, and hence it is evident that it was the hydrogen of the phenyl which was replaced by chlorine, bromine and hyponitric acid in the transformation of aniline into its chlorinated, brominated, &c. relatives.

This transformation is due to a secondary substitution affecting the hydrogen in the radical, which replaced the original ammonia-hydrogen; and the constitution of the substances in question may hence be graphically represented by the following formulæ :—

Chloraniline $\left\{\begin{matrix} H \\ H \\ C_{12}\begin{pmatrix} H_4 \\ Cl \end{pmatrix} \end{matrix}\right\}N$. Bromaniline $\left\{\begin{matrix} H \\ H \\ C_{12}\begin{pmatrix} H_4 \\ Br \end{pmatrix} \end{matrix}\right\}N$. Nitraniline $\left\{\begin{matrix} H \\ H \\ C_{12}\begin{pmatrix} H_4 \\ NO_4 \end{pmatrix} \end{matrix}\right\}N$.

Ethylochloraniline $\left\{\begin{matrix} H \\ C_4\ H_5 \\ C_{12}\begin{pmatrix} H_4 \\ Cl \end{pmatrix} \end{matrix}\right\}N$. Ethylobromaniline $\left\{\begin{matrix} H \\ C_4\ H_5 \\ C_{12}\begin{pmatrix} H_4 \\ Br \end{pmatrix} \end{matrix}\right\}N$. Ethylonitraniline $\left\{\begin{matrix} H \\ C_4\ H_5 \\ C_{12}\begin{pmatrix} H_4 \\ NO_4 \end{pmatrix} \end{matrix}\right\}N$.

Diethylochloraniline $\left\{\begin{matrix} C_4\ H_5 \\ C_4\ H_5 \\ C_{12}\begin{pmatrix} H_4 \\ Cl \end{pmatrix} \end{matrix}\right\}N$.

This mode of viewing their constitution is in perfect harmony with the facts at present in our possession, both as regards the deportment of the substitution-anilines, and the substances similarly derived from hydrated oxide of phenyl. Experiment has shown that in aniline 1, 2 or 3 equivalents of hydrogen may be replaced by chlorine, bromine, and probably also by the elements of hyponitric acid *. In these substances their basic properties gradually diminish with the successive insertions

* At the present moment we have only nitraniline, but it is scarcely to be doubted that we shall soon become acquainted with the nitro-term corresponding to dichloraniline and trichloraniline. Recent researches of M. Cahours (Ann. Ch. Phys. sér. xxvii. 439) on the derivatives of anisole have pointed out the first alkaloid containing 2 equivs. of hyponitric acid.

Anisidine ..... $C_{14}\ H_9\ \ NO_3$.

Nitranisidine ... $C_{14}\left\{\begin{matrix} H_8 \\ NO_4 \end{matrix}\right\}NO_3$.

Dinitranisidine $C_{14}\left\{\begin{matrix} H_7 \\ (NO_4)_2 \end{matrix}\right\}NO_3$.

In this series only the trinitranisidine $C_{14}\left\{\begin{matrix} H_6 \\ (NO_4)_3 \end{matrix}\right\}NO_3$ is wanting.

of chlorine or bromine into the compound. Bromaniline still retains a strongly alkaloidal character which in dibromaniline is so far impaired that by simple ebullition it is separated from its aqueous saline solutions; tribromaniline, lastly, is a perfectly indifferent compound. Now if we recollect that in monobrominated and dibrominated phenole (obtained by M. CAHOURS, by distilling respectively, bromosalicylic and dibromosalicylic acid), the original character of hydrated oxide of phenyl is gradually altered and becomes in tribromophenole (bromophenisic acid of M. LAURENT) powerfully acid, we cannot be surprised to find that the gradual development of electronegative properties in the radical should affect the nature of a basic system in which it replaces hydrogen. We have two parallel groups of bodies, the chemical character of which is differently affected by the modification induced in the radical, existing in both, by the assimilation of bromine.

Hydrated protoxide of phenyl	$HO, C_{12} H_5 O$, slightly acid.	Phenylamine	$\left.\begin{matrix} H \\ H \\ C_{12} H_5 \end{matrix}\right\} N$, powerfully basic.
Bromophenole	$HO, C_{12} \left\{\begin{matrix} H_4 \\ Br \end{matrix}\right\} O$, more so.	Bromophenylamine ...	$\left.\begin{matrix} H \\ H \\ C_{12} \left(\begin{matrix} H_4 \\ Br \end{matrix}\right) \end{matrix}\right\} N$, less so.
Dibromophenole ...	$HO, C_{12} \left\{\begin{matrix} H_3 \\ Br_2 \end{matrix}\right\} O$, more so.	Dibromophenylamine	$\left.\begin{matrix} H \\ H \\ C_{12} \left(\begin{matrix} H_3 \\ Br_2 \end{matrix}\right) \end{matrix}\right\} N$, less so.
Tribromophenole Bromophenisic acid	$HO, C_{12} \left\{\begin{matrix} H_2 \\ Br_3 \end{matrix}\right\} O$, powerfully acid.	Tribromophenylamine	$\left.\begin{matrix} H \\ H \\ C_{12} \left(\begin{matrix} H_2 \\ Br_3 \end{matrix}\right) \end{matrix}\right\} N$, neutral.

Tribromophenylamine (tribromaniline) is a compound differing in its nature in no way from oxamide. Both these substances are ammonia, whose basic character has been counterbalanced by the insertion of a powerfully electronegative radical in the place of one of the hydrogen-equivalents. These two substances, when subjected to the influence of strong acids, comport themselves in exactly the same manner; they both reproduce ammonia, the one with formation of tribromophenisic, the other of oxalic acid.

The paragraphs now following are devoted to a brief account of the bases derived from aniline by the insertion of methyl and amyl. I have not however followed out the examination of these substances to the same extent, the principle having been in fact sufficiently established by the formation of the ethyl bodies.

Action of Bromide and Iodide of Methyl upon Aniline.

Methylaniline (*Methylophenylamine*).

The deportment of aniline with bromide of methyl resembles its behaviour with the ethyl-compound. The mixture rapidly solidifies into a crystalline mass of hydrobromate of methylaniline. Bromide of methyl being extremely volatile, I have used also the iodide, which boils at a more convenient temperature. The action of the latter compound upon aniline is very remarkable, the evolution of heat, on mixing the two substances, being so great, that the liquid enters into violent ebullition, so that unless the substances be mixed gradually, the crystalline hydriodate, which is formed immediately, is actually thrown out of the vessel.

Methylaniline, when separated from the hydrobromate or hydriodate, appears as a transparent oil of a peculiar odour, somewhat different from that of aniline, and boiling at 192°; it has retained the properties of aniline in a higher degree than the ethylated compound. This substance yields still the blue coloration with hypochlorite of lime, although in a less degree than aniline. Its salts are less soluble than those of ethylaniline; they are at once formed in the crystalline state on addition of the respective acids; the oxalate crystallizes very easily, but is rapidly decomposed with reproduction of aniline, and probably with formation of oxalate of methyl*.

The composition of methylaniline is represented by the expression

$$C_{14}\,H_9\,N=C_{12}\left\{\begin{matrix}H_6\\C_2\,H_3\end{matrix}\right\}N=\left\{\begin{matrix}H\\C_2\;H_3\\C_{12}\;H_5\end{matrix}\right\}N.$$

I have established this formula by the analysis of the platinum-salt. This is precipitated as a transparent oil, which rapidly changes into pale-yellow crystalline tufts, resembling the corresponding aniline-salt, but liable to rapid decomposition. The washing must be quickly done, for the salt is extremely soluble in water, and must be immediately followed by desiccation. Even when very carefully prepared, it has become dark by the time it is ready for combustion. It turns instantaneously black if an alcoholic solution of the hydrochlorate be employed for its preparation.

Analysis I. refers to a salt obtained with the base prepared by means of the bromide; for analysis II. the base had been formed by the iodide. The specimen analysed under III. again had been obtained with the bromide, but it was in an advanced state of decomposition, and had in consequence become perfectly black.

I. 0·1018 grm. of platinum-salt gave 0·0319 grm. of platinum.
II. 0·2467 grm. of platinum-salt gave 0·0784 grm. of platinum.
III. 0·2065 grm. of platinum-salt gave 0·0660 grm. of platinum.

* The aniline thus reproduced was identified by the analysis of the platinum-compound.
0·7910 grm. of platinum-salt gave 0·2615 grm. of platinum.

Experimental.	Theoretical percentage of platinum in aniline-platinum-salt.
33·05	32·98

Percentage of platinum.		
I.	II.	III.
31·33	31·78	31·96.

The formula

$$C_{14}\,H_9\,N,\,H\,Cl,\,Pt\,Cl_2$$

requires the following values:—

	Theory.		Mean of I. and II.
1 equiv. of Methylaniline . .	107·00	34·16	——
1 equiv. of Hydrochloric acid.	36·50	11·65	——
2 equivs. of Chlorine . . .	71·00	22·67	——
1 equiv. of Platinum	98·68	31·52	31·55
1 equiv. of Platinum-salt . .	313·18	100·00	

I have not attempted to form a dimethylaniline.

Action of Iodide of Methyl upon Ethylaniline.

Methylethylaniline (*Methylethylophenylamine*).

I have established the existence of this compound merely by qualitative experiments. The mixture of ethylaniline and iodide of methyl begins to crystallize after two days' exposure to the temperature of boiling water. Methylethylaniline resembles the preceding base in its odour, but has no longer any action upon hypochlorite of lime. I had not prepared a sufficient quantity of the compound for a determination of the boiling-point. The salts of this base are extremely soluble. With the exception of the hydrobromate, I have not been able to obtain a single one in crystals. Even the platinum-salt is not to be obtained in the crystalline form; it is extremely soluble, and separates, if very concentrated solutions be employed, as a yellow oil, which does not solidify even after lengthened exposure to the air. This circumstance has prevented me from fixing the composition of methylethylaniline by a number.

It cannot however be doubted that it is represented by the formula—

$$C_{18}\,H_{13}\,N = C_{12}\left\{\begin{matrix} H_5 \\ C_2\,H_3 \\ C_4\,H_5 \end{matrix}\right\} N = \left\{\begin{matrix} C_2\;\;H_3 \\ C_4\;\;H_5 \\ C_{12}\,H_8 \end{matrix}\right\} N.$$

This compound presents a certain degree of interest, inasmuch as the 3 equivs. of hydrogen in the ammonia are replaced by three different radicals, namely by methyl, ethyl and phenyl. I have prepared however a similar compound containing, instead of methyl, amyl, whose properties permitted an easier analysis.

Action of Bromide of Amyl upon Aniline.

Amylaniline (*Amylophenylamine*).

A mixture of aniline and an excess of bromide of amyl, when left in contact at the common temperature for some days, deposits magnificent crystals of hydrobromate of aniline. Never have I obtained this salt in larger and more definite crystals; although I have seen it deposited of late from a good many solutions. The mother-liquor of this salt is a mixture of amylaniline and bromide of amyl. If aniline be heated in the water-bath with a very large excess of bromide of amyl, the whole is converted into hydrobromate of amylaniline, which remains dissolved in the excess of bromide.

When prepared without the co-operation of heat, the amylaniline may be purified simply by separating the crystals of the aniline-salt and distilling the remaining mixture, when the bromide of amyl passes over long before the amyl-base begins to volatilize. If the base has been produced by heating the mixture, it is necessary, after the excess of bromide has been removed, to distil the hydrobromate with potassa. On submitting the base, purified in the usual manner, to combustion, the following numbers were obtained:—

0·2760 grm. of oil gave 0·8161 grm. of carbonic acid, and 0·2560 grm. of water.

This analysis leads to the formula—

$$C_{22}H_{17}N = C_{12}\left\{\begin{matrix} H_6 \\ C_{10}H_{11}\end{matrix}\right\}N = \left\{\begin{matrix} H \\ C_{10}H_{11} \\ C_{12}H_5\end{matrix}\right\}N,$$

as may be seen from a juxtaposition of the theoretical and experimental values.

	Theory.		Experiment.
22 equivs. of Carbon	132	80·98	80·64
17 equivs. of Hydrogen	17	10·42	10·30
1 equiv. of Nitrogen	14	8·60	——
1 equiv. of Amylaniline	163	100·00	

Amylaniline is a colourless liquid, possessing all the family-features of the group. It is distinguished, at the common temperature, by a very agreeable, somewhat rose-like odour, rather an unusual property for an amyl-compound; however, it does not deny its origin, for on heating the base the disgusting odour of the fusel-alcohol appears but slightly modified. Amylaniline boils constantly at 258°, or $54 = 3 \times 18°$ higher than ethylaniline. This boiling-point is characteristic, inasmuch as the elementary group amyl raises the boiling-point of aniline 44° higher than does the insertion of two equivalents of ethyl, whose weight is not very inferior to that of the single amyl-equivalent.

The amyl-base forms beautiful rather insoluble salts with hydrochloric, hydro-

bromic and oxalic acids; when heated with water, they form an oily layer on the surface, and crystallize only slowly on cooling: they have the peculiar fatty appearance which characterizes the crystalline amyl-compounds. The platinum-salt is precipitated as a yellow mass of an unctuous consistence; it crystallizes but very slowly, and usually not before partial decomposition has set in. It is on this account that I have not made an analysis of this compound.

Action of Bromide of Amyl upon Amylaniline.

Diamylaniline (*Diamylophenylamine*).

A mixture of amylaniline and bromide of amyl solidifies after two days' exposure to the temperature of the water-bath. The new basic compound, when separated and purified in the usual manner, resembles the preceding base, especially with respect to odour. Its salts are so insoluble in water that at the first glance one is almost inclined to doubt the basicity of the substance, inasmuch as the oil appears to be perfectly insoluble in dilute hydrochloric and sulphuric acids. However, the oily drops floating in the acid solution are the salts themselves, which gradually solidify into splendid crystalline masses, having likewise the fatty appearance of amyl-substances. The composition of diamylaniline is represented by the expression—

$$C_{32}H_{27}N = C_{12}\left\{\begin{matrix} H_5 \\ C_{10}H_{11} \\ C_{10}H_{11}\end{matrix}\right\}N = \left\{\begin{matrix} C_{10}H_{11} \\ C_{10}H_{11} \\ C_{12}H_5\end{matrix}\right\}N.$$

I have established this formula by the analysis of the platinum-compound, which is precipitated as an oily mass, rapidly solidifying into a brick-red crystalline substance. If an alcoholic solution of the hydrochlorate be employed, it is immediately obtained in the crystalline state. When exposed to the heat of the water-bath this salt fuses, without however undergoing any decomposition.

On analysis the following results were obtained:—

I. 0·3015 grm. of platinum-salt gave 0·4820 grm. of carbonic acid, and 0·1765 grm. of water.

II. 0·2550 grm. of platinum-salt gave 0·0572 grm. of platinum.

III. 0·4750 grm. of platinum-salt gave 0·1061 grm. of platinum.

	Percentage.		
	I.	II.	III.
Carbon	43·60	——	——
Hydrogen	6·50	——	——
Platinum	——	22·43	22·34

The formula

$$C_{32}H_{27}N, HCl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
32 equivs. of Carbon	192·00	43·71	43·60
28 equivs. of Hydrogen . . .	28·00	6·37	6·50
1 equiv. of Nitrogen	14·00	3·19	——
3 equivs. of Chlorine	106·50	24·25	——
1 equiv. of Platinum	98·68	22·47	22·38
1 equiv. of Platinum-salt . .	439·18	100·00	

Diamylaniline boils between 275° and 280°: the small scale upon which I had to work prevented me from determining it more accurately. It is interesting to see how very little the boiling-point is raised by the introduction of the second equivalent of amyl, when compared with the effect produced by the insertion of the first. The same remark applies to the ethylanilines.

Action of Bromide of Ethyl upon Amylaniline and of Bromide of Amyl upon Ethylaniline.

Amylethylaniline (*Amylethylophenylamine*).

It remained now only to analyse a basic compound in which the three equivalents of the ammonia-hydrogen should be replaced by three different radicals. I found in amylethylaniline a substance similar in composition to methylethylaniline, but which by its properties admitted of a rigorous analytical examination.

Amylethylaniline is formed without difficulty by the action of bromide of ethyl upon amylaniline. The mixture having been exposed to the heat of the water-bath, the conversion was found to be complete after two days. When purified in the usual way, amylethylaniline forms a colourless oil, boiling at 262°, only 4° higher than the amyl-base. The properties of this substance are analogous to those of the other bases. It forms a beautiful crystalline hydrochlorate and hydrobromate; the platinum-salt is precipitated in form of a light orange-yellow pasty mass, which rapidly crystallizes. This salt fuses at 100°. By analysis of the platinum-compound I was enabled to fix without difficulty the composition of the base, which is represented by the formula

$$C_{26}H_{21}N=C_{12}\left\{\begin{matrix}H_5\\C_4\ H_5\\C_{10}H_{11}\end{matrix}\right\}N=\left\{\begin{matrix}C_4\ H_5\\C_{10}H_{11}\\C_{12}H_5\end{matrix}\right\}N.$$

I. 0·2893 grm. of platinum-salt gave 0·4137 grm. of carbonic acid, and 0·1495 grm. of water.

II. 0·2647 grm. of platinum-salt gave 0·0652 grm. of platinum.

III. 0·2510 grm. of platinum-salt gave 0·0619 grm. of platinum.

	Percentage-composition.		
	I.	II.	III.
Carbon	39·00	——	——
Hydrogen	5·70	——	——
Platinum	——	24·63	24·66

The formula

$$C_{26}\,H_{21}\,N,\,H\,Cl,\,Pt\,Cl_2$$

requires the following values:—

	Theory.		Experiment.
26 equivs. of Carbon	156·00	39·27	39·00
22 equivs. of Hydrogen . . .	22·00	5·54	5·70
1 equiv. of Nitrogen	14·00	3·53	——
3 equivs. of Chlorine	106·50	26·81	——
1 equiv. of Platinum	98·68	24·84	24·64
1 equiv. of Platinum-salt . . .	397·18	100·00	

A substance of exactly the same composition as amylethylaniline may be obtained by the action of bromide of amyl upon ethylaniline. I was led to prepare this compound by some ideas which had suggested themselves in a perfectly different line of experiments. I wished to ascertain whether the several hydrogen-equivalents in ammonia were of the same value, if I may use this expression, or in other words, whether it was indifferent which of the three equivalents was replaced by a given radical. Supposing that in ammonia

$$\left.\begin{matrix} a\,H \\ b\,H \\ c\,H \end{matrix}\right\} N,$$

it is the *a* hydrogen which is replaced by phenyl, the question arose whether the same substance would be formed, for instance, by substituting amyl and ethyl, either for *b* and *c*, or for *c* and *b*.

I have carefully compared the properties of amylethylaniline, by which name I designate the compound produced by the action of bromide of ethyl upon amylaniline with those of ethylamylaniline obtained by acting with bromide of amyl upon ethylaniline, and find that these substances comport themselves in every respect perfectly alike.

A last and decisive argument was hoped to be gained from the deportment of the salts of these bases, when subjected to the influence of heat. For this purpose the hydrobromates were prepared. When distilled, both these salts were split into bromide of amyl and ethylaniline; I hence assume that the action of bromide of ethyl upon amylaniline, and that of bromide of amyl upon ethylaniline, give rise to the formation of exactly the same basic compound.

Action of Bromide of Ethyl upon Ammonia.

After the termination of the experiments which have been detailed in the preceding pages, there remained no doubt in my mind respecting the deportment which ammonia itself would exhibit when subjected in a similar manner to the influence of bromide of ethyl. I had a right to expect in this reaction the consecutive formation of three alkaloids, differing from ammonia by containing respectively one, two or the three equivalents of hydrogen replaced by ethyl.

Experiment has realized this expectation in a very satisfactory manner. I intend to give here only an outline of the process employed, and a short description of the substances obtained, together with some characteristic numbers, fixing beyond a doubt the composition of the new bases formed under these circumstances. I hope that I shall soon be able to communicate a more detailed account of these compounds, as well as of the bases belonging to the methyl- and amyl-series.

Formation of Ethylamine (*Ethylammonia*).

Bromide of ethyl acts very slowly on an aqueous solution of ammonia in the cold. Action however takes place; after the lapse of a week or ten days the solution contains a considerable quantity of a hydrobromate in solution. This hydrobromate is a mixture of the salts of ammonia and ethylamine, the base discovered by M. Wurtz on decomposing cyanate of ethyl with potassa. The presence of this compound may be readily proved by evaporating the liquid, after the separation of the excess of bromide of ethyl, to dryness in the water-bath, in order to drive off alcohol which might have possibly been formed. On adding potassa-solution to the solid residue, an alkaline gas is at once evolved, which burns with the pale-blue flame of ethylamine.

If an alcoholic solution of ammonia be substituted for the aqueous liquid, the decomposition proceeds more rapidly. After twenty-four hours a copious crystalline precipitate of bromide of ammonium has been deposited. The mother-liquor contains hydrobromate of ethylamine and the base in the free state.

The action of bromide of ethyl upon ammonia may be considerably accelerated by raising the temperature to the boiling-point of water. I found it convenient to introduce a concentrated solution of ammonia, with an excess of bromide of ethyl, into pieces of combustion-tube 2 feet in length. These tubes, after having been carefully sealed before the blowpipe, were immersed to the height of about half a foot into boiling water. The bromide of ethyl enters at once into lively ebullition, rises through the supernatant layer of ammonia, condenses in the upper part of the tube, which is cold, and falls down to commence again the same circulation. During this process the bromide of ethyl diminishes rapidly in volume. The reaction may be considered terminated as soon as a quarter of an hour's ebullition ceases to effect a considerable change in the bulk of the bromide. On opening the tube, the solution

is found to be either neutral or even of an acid reaction, and to contain hydrobromate of ethylamine, which may be separated, by distillation with potassa, with all the properties enumerated by M. Wurtz. I have not to add a single word to the accurate description of this distinguished chemist, and will here only give the analysis of a platinum-salt prepared with ethylamine which had been obtained by this process:—

0·2521 grm. of platinum-salt gave 0·0992 grm. of platinum.

The formula

$$C_4H_7N, HCl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Ethylamine . . .	45·00	17·91	——
1 equiv. of Hydrochloric acid .	36·50	14·55	——
2 equivs. of Chlorine	70·00	28·24	——
1 equiv. of Platinum	98·68	39·30	39·34
1 equiv. of Platinum-salt . . .	260·18	100·00	

The production of ethylamine in this reaction is absolutely analogous to that of ethylaniline; it is represented by the equation

$$H_3N+C_4H_5Br=C_4H_7N, HBr.$$

Formation of Diethylamine (Diethylammonia).

On treating an aqueous solution of ethylamine in the same manner with an excess of bromide of ethyl, phenomena of a perfectly analogous character are observed. The reaction however proceeds more rapidly and is terminated after a few hours' ebullition. The aqueous layer, which assumes a bright yellow colour, deposits acicular crystals on cooling, consisting of the hydrobromate of a new base, for which I propose the name diethylamine or diethylammonia. This base may be readily separated by distillation with potassa, when it passes over in form of a very volatile and inflammable liquid, which is still extremely soluble in water and of a powerful alkaline reaction. When dissolved in hydrochloric acid and mixed with a concentrated solution of bichloride of platinum, it yields a very soluble platinum-salt, which crystallizes in orange-red grains, very different from the orange-yellow leaves of the corresponding ethylamine-salt.

The analysis of this platinum-salt shows that diethylamine may be viewed as ammonia, in which 2 equivs. of hydrogen are replaced by 2 of ethyl.

0·2250 grm. of platinum-salt gave 0·1430 grm. of carbonic acid, and 0·0890 grm. of water.

0·3413 grm. of platinum-salt gave 0·1210 grm. of platinum.

These numbers agree exactly with the formula

$$C_8H_{11}N, HCl, PtCl_2,$$

which requires the following values:—

	Theory.		Experiment.
8 equivs. of Carbon	48·00	17·19	17·33
12 equivs. of Hydrogen . . .	12·00	4·30	4·39
1 equiv. of Nitrogen	14·00	5·03	——
3 equivs. of Chlorine	106·50	38·14	——
1 equiv. of Platinum	98·68	35·34	35·45
1 equiv. of Platinum-salt. . .	279·18	100·00	

The preceding analyses establish the composition of diethylamine, which is represented by the formula

$$C_8 H_{11} N = \left\{ \begin{matrix} H \\ C_4 H_5 \\ C_4 H_5 \end{matrix} \right\} N.$$

Formation of Triethylamine (*Triethylammonia*).

This arises from diethylamine in the same manner as the latter from ethylamine: however unlike the deportment observed in the formation of diethylaniline, the rapidity of the action increases with the progress of the ethylation. A mixture of a concentrated solution of diethylamine with bromide of ethyl solidifies after a very short ebullition into a mass of beautiful fibrous crystals, sometimes of several inches in length, being the hydrobromate of a new base, for which I propose the name of triethylamine or triethylammonia. This alkaloid may be readily separated by distillation with potassa, when it presents itself in the form of a light, colourless, powerfully alkaline liquid, still very volatile and inflammable, and also pretty soluble in water, but in a less degree than diethylamine.

To fix the composition of triethylamine, the platinum-salt was subjected to analysis. This is one of the finest salts which I have ever seen. It is extremely soluble in water, and crystallizes on the cooling of concentrated solutions in magnificent orange-red rhombic crystals, which are obtained of perfect regularity and of very considerable size (half an inch in diameter), even if very limited quantities of solution be employed. The analysis of this salt, which slightly fused at 100°, shows that triethylamine may be considered as ammonia, in which the 3 equivs. of hydrogen are replaced by 3 of ethyl.

I. 0·5950 grm. of platinum-salt gave 0·5110 grm. of carbonic acid, and 0·2800 grm. of water.

II. 0·1860 grm. of platinum-salt gave 0·0595 grm. of platinum.

III. 0·5230 grm. of platinum-salt gave 0·1679 grm. of platinum.

	Percentage-composition.		
	I.	II.	III.
Carbon	23·42	——	——
Hydrogen	5·22	——	——
Platinum	——	31·99	32·10

The formula

$$C_{12}H_{15}N, HCl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
12 equivs. of Carbon	72·00	23·43	23·42
16 equivs. of Hydrogen . . .	16·00	5·20	5·22
1 equiv. of Nitrogen	14·00	4·54	——
3 equivs. of Chlorine	106·50	34·71	——
1 equiv. of Platinum	98·68	32·12	32·04
1 equiv. of Platinum-salt . .	307·18	100·00	

These numbers are sufficient to establish beyond a doubt the formula

$$C_{12}H_{15}N = \left\{\begin{matrix} C_4H_5 \\ C_4H_5 \\ C_4H_5 \end{matrix}\right\} N,$$

as representing the compound in question.

Although not inclined to expect a farther action of bromide of ethyl upon triethylamine, after the experiments performed with diethylaniline, but hoping to obtain in this series more definite results than the latter had yielded, I thought it important to appeal once more to experiment. A mixture of an aqueous solution of triethylamine and bromide of ethyl, sealed for this purpose into a tube, solidified after two hours' ebullition. The crystals formed in this reaction had the fibrous aspect of the hydrobromate of triethylamine; still among the transparent prisms some white opake granular crystals were observed. To gain more positive information, the excess of bromide of ethyl was volatilized and the residue distilled with potassa. The base obtained in this manner, converted into a platinum-salt and submitted in this form to analysis—

0·1040 grm. of platinum-salt left 0·0334 grm. of platinum.

Experimental percentage.	Theoretical percentage in the platinum-salt of triethylamine.
32·11	32·11

Accordingly, the base which had distilled over, had evidently not been affected any farther by the influence of bromide of ethyl. The appearance however of the opake crystals indicates that a second compound is formed, whose careful study is necessary for the elucidation of this reaction. I am at present engaged with this part of the inquiry.

The action then of bromide of ethyl upon ammonia gives rise to the formation of the following series of compounds:—

Ammonia . . . . $H_3 N = \left\{ \begin{matrix} H \\ H \\ H \end{matrix} \right\} N.$

Ethylamine (Ethylammonia) $C_4 H_7 N = \left\{ \begin{matrix} H \\ H \\ C_4 H_5 \end{matrix} \right\} N.$

Diethylamine (Diethylammonia) $C_8 H_{11} N = \left\{ \begin{matrix} H \\ C_4 H_5 \\ C_4 H_5 \end{matrix} \right\} N.$

Triethylamine (Triethylammonia) $C_{12} H_{15} N = \left\{ \begin{matrix} C_4 H_5 \\ C_4 H_5 \\ C_4 H_5 \end{matrix} \right\} N.$

It cannot be doubted for a moment that the same compounds will be obtained in the methyl- and amyl-series, the first terms in each of these series having been actually prepared by M. Wurtz. Nor is it improbable that arsenietted and phosphoretted hydrogen, which, as is well known, imitate to a certain extent the habits of ammonia, when subjected to the action of the chlorides, bromides or iodides of the alcohol-radicals, will yield a series of arsenietted or phosphoretted bases, corresponding to the three classes observed with nitrogen. The highly remarkable bodies discovered by M. Paul Thenard appear to warrant this expectation as far as the phosphorus-series is concerned, his compound

$$C_6 H_9 P$$

corresponding evidently in the phosphoretted methyl-series to triethylamine. I mean to extend these researches to the action of the bromides of the alcohol-radicals on phosphoretted and arsenietted hydrogen.

In the preceding pages, I have only endeavoured to establish the composition and the principal physical characters of the new compounds which form the subject of this investigation. To complete their history, it will be necessary to submit to a careful examination their deportment under the influence of the ordinary decomposing agents, and also their behaviour with other organic substances. The study of the imidogen- and nitrile-bases, to use this convenient though only provisional designation, will require particular attention, the character of the amidogen-bases being already pretty well established by the numerous researches respecting aniline, which have been performed within the last few years. We cannot but expect, that, although the general character of all these substances is very nearly the same, their special properties must present considerable diversity, which may be clearly defined by, and even anticipated from, the theoretical conception of their constitution, as deduced from the present investigation. Though fully aware of the dangers threatening the

inquirer as soon as he steps beyond the interpretation of well-established facts, it is difficult to resist the temptation of indulging even now in some speculations on the probable deportment of these alkaloids. In a former paper* I have pointed out that the methods which convert the ammonia-salts into nitriles, fail to produce a similar effect upon the salts of aniline, while experiment has shown that these salts are capable of producing compounds analogous to the amides, to the amidogen-acids and to the imides. This result is perfectly intelligible if we conceive aniline in the light of an amidogen-base. In the same manner we shall probably see that the imidogen-bases, such as ethylaniline and diethylamine, although still capable of giving rise to the formation of amides and amidogen-acids, will yield no longer compounds representing the imides of the ammonia-salts; in the nitrile-bases, lastly, such as diethylaniline or triethylamine, we shall probably find that the faculty of yielding derivatives by elimination of water is either restricted to the formation of compounds corresponding to the so-called amidogen-acids, or has entirely disappeared.

Relation of the bases derived from Aniline and Ammonia with other groups of Alkaloids.

It is impossible to leave the history of these compounds without alluding to some remarkable relations existing between these substances and other bodies of an analogous character, whose constitution is likely to be illustrated by this line of researches. The basic substances derived from aniline, when expressed in formulæ excluding any peculiar view respecting the mode in which the elements are arranged, present a series which is exhibited in the following synoptical table:—

Aniline	$C_{12}H_7N=$
Methylaniline	$C_{14}H_9N=C_{12}H_7N+C_2H_2$
Ethylaniline	$C_{16}H_{11}N=C_{12}H_7N+2C_2H_2$
Methylethylaniline . . .	$C_{18}H_{13}N=C_{12}H_7N+3C_2H_2$
Diethylaniline	$C_{20}H_{15}N=C_{12}H_7N+4C_2H_2$
Amylaniline	$C_{22}H_{17}N=C_{12}H_7N+5C_2H_2$
Ethylamylaniline	$C_{26}H_{21}N=C_{12}H_7N+7C_2H_2$
Diamylaniline	$C_{32}H_{27}N=C_{12}H_7N+10C_2H_2$

This table shows that the alkaloids in question differ from each other by nC_2H_2, the elementary difference of the various alcohols and their derivatives; we perceive moreover that the series ascends regularly up to the term $C_{12}H_7N+5C_2H_2$, when the compound $C_{12}H_7N+6C_2H_2$ is wanting; lastly, we miss the terms $C_{12}H_7N+8C_2H_2$ and $C_{12}H_7N+9C_2H_2$. The first gap might be easily filled by submitting amylaniline to the action of iodide of methyl, methylamylaniline being in fact $C_{24}H_{19}N=C_{12}H_7N+6C_2H_2$. The other wanting terms cannot be reached from aniline before some of the missing alcohols are discovered.

* Chem. Soc. Quart. Journ. ii. p. 331.

On examining more closely the formulæ of the preceding conspectus, we find that several of them represent basic compounds previously known. Chemists are acquainted with the beautiful reaction by which ZININ first linked aniline to benzole through nitrobenzole.

$\underbrace{C_{12}H_6}_{\text{Benzole.}}$ $\underbrace{C_{12}H_5NO_4}_{\text{Nitrobenzole.}}$ $\underbrace{C_{12}H_7N.}_{\text{Aniline.}}$

Researches performed in the most different departments of organic chemistry have gradually elicited a series of carbohydrides differing from benzole by n C_2H_2, and each of these terms, when treated with nitric acid, and subsequently exposed to the action of reducing agents, has yielded its corresponding base. We are now in the possession of the following series of alkaloids derived from hydrocarbons:—

Benzole	$C_{12}H_6$	Aniline	$C_{12}H_7N$
Toluole	$C_{14}H_8 = C_{12}H_6 + C_2H_2$	Toluidine	$C_{14}H_9N = C_{12}H_7N + C_2H_2$
Xylole	$C_{16}H_{10} = C_{12}H_6 + 2C_2H_2$	Xylidine*	$C_{16}H_{11}N = C_{12}H_7N + 2C_2H_2$
Cumole	$C_{18}H_{12} = C_{12}H_6 + 3C_2H_2$	Cumidine†	$C_{18}H_{13}N = C_{12}H_7N + 3C_2H_2$
Cymole	$C_{20}H_{14} = C_{12}H_6 + 4C_2H_2$	Cymidine‡	$C_{20}H_{15}N = C_{12}H_7N + 4C_2H_2$

On comparing the formulæ of the bases contained in the last table with those representing the alkaloids derived from aniline by the introduction of methyl and ethyl, we find that they exactly coincide. Toluidine has the same composition as methylaniline; xylidine, cumidine and cymidine are represented by the same formulæ as ethylaniline, methylethylaniline and diethylaniline. The question then arises, are these substances identical, or are they only isomeric with each other? I have carefully compared the properties of toluidine with those of methylaniline, and also methylethylaniline with cumidine. These substances are not identical, but only isomeric. The most striking dissimilarity we observe in the characters of toluidine and methylaniline. The former is a beautiful crystalline compound, boiling at 198°, yielding difficultly soluble, perfectly stable salts with almost all acids, and a splendid orange-yellow platinum-salt, which may be boiled without decomposition. We are unacquainted with any process by which we could convert this body into aniline. Methylaniline, on the other hand, is an oily liquid, boiling at 192°, whose salts are distinguished by their solubility and by the facility with which they are decomposed, aniline being reproduced (*vide* p. 113). The platinum-salt, even when freshly precipitated, is of a pale-yellow colour, which immediately darkens, turning perfectly black after the lapse of an hour. Scarcely less striking is the dissimilarity of cumidine and methylethylaniline, although in this case both substances are liquids. For

* Unpublished researches of M. CAHOURS. This chemist has lately found the long-wanted carbohydride $C_{16}H_{10}$, among the products of the distillation of wood. It comports itself exactly like benzole and its congeners, yielding nitroxylole and xylidine.

† On Cumidine, a new Organic Base, by E. CHAMBERS NICHOLSON, Chem. Soc. Quart. Journ. i. 1.

‡ This compound has been partly investigated by Mr. NOAD.

details I refer to Mr. Nicholson's* paper on Cumidine, and to what I have stated about methylethylaniline (*vide* p. 114). The quantity of this substance I had at my disposal was not sufficient for a determination of the boiling-point; but if we recollect that ethylaniline boils at 204°, and that the introduction of methyl into aniline raised its boiling-point about 10°, it is evident that methylethylaniline cannot boil at a temperature much higher than 214°, *i. e.* eleven degrees below 225°, the boiling-point of cumidine observed by Mr. Nicholson. An account of the properties of xylidine has not yet been published; however, I have not the slightest doubt that M. Cahours will find them widely differing from those of ethylaniline.

Toluidine, xylidine and cumidine, resembling aniline, not only in their physical characters, but also in their origin from carbohydrides, evidently belong to the class of alkaloids for which I have provisionally retained the name amidogen-bases, while the basic compounds derived from aniline are either imidogen- or nitrile-bases. The difference of properties depends upon a difference in the molecular construction, as represented graphically by the following table:—

$$\left.\begin{matrix} H \\ H \\ C_{12}H_5 \end{matrix}\right\} N = \text{Aniline.}$$

$$\left.\begin{matrix} H \\ H \\ C_{14}H_7 \end{matrix}\right\} N = \text{Toluidine} = C_{14}H_9\,N = \text{Methylaniline} = \left\{\begin{matrix} H \\ C_2H_3 \\ C_{12}H_5 \end{matrix}\right\} N.$$

$$\left.\begin{matrix} H \\ H \\ C_{16}H_9 \end{matrix}\right\} N = \text{Xylidine} = C_{16}H_{11}\,N = \text{Ethylaniline} = \left\{\begin{matrix} H \\ C_4H_5 \\ C_{12}H_5 \end{matrix}\right\} N.$$

$$\left.\begin{matrix} H \\ H \\ C_{18}H_2 \end{matrix}\right\} N = \text{Cumidine} = C_{18}H_{13}\,N = \text{Methylethylaniline} = \left\{\begin{matrix} C_2H_3 \\ C_4H_5 \\ C_{12}H_5 \end{matrix}\right\} N.$$

These formulæ assume the existence of a series of homologous radicals of compounds resembling in their chemical deportment, to a certain extent, the alcohols of the series $C_nH_{n+2}O_2$. In a former paper†, I have shown how this resemblance becomes more and more marked with every new investigation performed in this department of the science. A judicious application to these substances of the various methods hitherto employed in combining the radicals of the common alcohols with bromine or iodine, will probably enable us before long to obtain the corresponding products in the phenyl-, toluyl-, xylyl- and cumyl-series. The discovery of these substances will furnish us at once with new processes for the production of the basic compounds in question, for it cannot be doubted that their action upon ammonia will give rise to the formation of the respective alkaloids with the same facility with which the treatment of ammonia with bromide and iodide of ethyl induces the form-

* *Loc. cit.* p. 125.

† Chem. Soc. Quart. Journ. ii. p. 329.

ation of ethylamine; we may hope moreover to form the imidogen- and nitrile-terms of these radicals, in the phenyl-series for instance:—

$$\left.\begin{matrix} H \\ C_{12}H_5 \\ C_{12}H_5 \end{matrix}\right\} N, \text{ Diphenylamine} \quad \text{and} \quad \left.\begin{matrix} C_{12}H_5 \\ C_{12}H_5 \\ C_{12}H_5 \end{matrix}\right\} N, \text{ Triphenylamine,}$$

the production of which, as mentioned in the commencement of this paper, I have in vain attempted by the action of the phenyl-alcohol at high temperatures upon aniline.

The view which I propose in the preceding remarks respecting the constitution of toluidine, xylidine and cumidine, must as yet be considered as a mere hypothesis. It will not however be difficult to establish it by facts. The action of bromide of ethyl upon these substances will at once decide this question. These bases, when subjected to the influence of the bromides, will give rise to the formation of a series of bases similar to those which I have obtained from aniline. I may mention that the deportment of toluidine and cumidine, in this respect, is now being studied by several of my pupils. There is no difficulty in introducing 1 equiv. of ethyl into toluidine; the experiments are however not yet sufficiently advanced as to affirm also the insertion of the second equivalent. The alkaloid obtained by acting with bromide of ethyl upon toluidine is represented by the formula

$$C_{18}H_{13}N,$$

so that we are now in possession of three alkaloids of exactly the same composition, namely, ethylotoluidine, methylethylaniline and cumidine; and here I cannot but allude to the wonderful variety of isomeric compounds to which a continuation of these researches must necessarily lead. We see at a glance that substances of the formula

$$C_{18}H_{13}N$$

will also be obtained by inserting 1 equiv. of methyl into xylidine, by introducing 2 equivs. of methyl into toluidine, or by fixing upon aniline the radical (propyl) belonging to the missing alcohol of propionic acid* (metacetic acid). We thus arrive at six alkaloids, having all the same numerical formulæ, but widely differing in their construction.

* A more appropriate name for metacetic acid, proposed by Dumas, Malaguti and Leblanc (Compt. Rend. xxv. 656), as it is the *first* acid of the series $C_nH_nO_4$ that exhibits the character of a *fatty* acid, *i. e.* in being separated from solution as a layer of oil, and in forming salts with the alkalies that have a greasy appearance.

$$\left.\begin{array}{ll}
\text{Cumidine} & \left\{\begin{matrix} H \\ H \\ C_{18}H_{11}\end{matrix}\right\}N \\
\text{Methyloxylidine} & \left\{\begin{matrix} H \\ C_2H_3 \\ C_{16}H_9\end{matrix}\right\}N \\
\text{Ethylotoluidine} & \left\{\begin{matrix} H \\ C_4H_5 \\ C_{14}H_7\end{matrix}\right\}N \\
\text{Dimethylotoluidine} & \left\{\begin{matrix} C_2H_3 \\ C_2H_3 \\ C_{14}H_7\end{matrix}\right\}N \\
\text{Propylaniline} & \left\{\begin{matrix} H \\ C_6H_7 \\ C_{12}H_5\end{matrix}\right\}N \\
\text{Methylethylaniline} & \left\{\begin{matrix} C_2H_3 \\ C_4H_5 \\ C_{12}H_5\end{matrix}\right\}N
\end{array}\right\} = C_{18}H_{13}N.$$

This multiplicity of course augments in the same measure as we ascend upon the scale of organic compounds. For every step the number of possible isomeric bases increases by two, so that on arriving at the term diamylaniline,

$$C_{32}H_{27}N,$$

being the last member (*vide* p. 124) in the aniline-series which I have examined, we find that its numerical formula actually represents not less than twenty different alkaloids which the progress of science cannot fail to call into existence,—a striking illustration of the simplicity in variety that characterizes the creations of organic chemistry.

Not less numerous will be the isomerisms in the series of bases derived by the insertion into ammonia of the alcohol-radicals C_nH_{n+1} only, as soon as the group of these alcohols themselves shall be more completely known. Ethylamine is isomeric with dimethylamine; diethylamine has the same composition as methylopropylamine, a base containing ethyl and propyl, the alcohol-radical in the propionic (metacetic) series, as dimethylethylamine, and lastly, as butylamine. Some chemists are actually inclined to consider as such a volatile alkaloid discovered by Dr. ANDERSON* among the products of the distillation of animal substances, and described by him under the name of petinine. The formula established by Dr. ANDERSON is

$$C_8H_{10}N;$$

but it is not unlikely that on repeating the analysis an additional hydrogen-equivalent

* Transactions of the Royal Society of Edinburgh, xvi. 4.

will be found. The boiling-point of the compound (75°) is very much in favour of butylamine*.

In a similar manner a great number of bases identical in composition with triethylamine will soon be found; capronamine, methylamylamine, ethylobutylamine, dipropylamine, and a number of others.

In concluding this paper, which, from the great number of experimental details which I had to bring forward, has been swelled almost beyond legitimate dimensions, I cannot but allude to the aid which the study of the natural alkaloids may possibly derive from a prosecution of these researches. I am, as I have said, far from believing that the constitution of substances, like quinine and morphine, is as simple as that of the bases described in the preceding memoir; we know that the typical system

$$\left.\begin{matrix} X \\ Y \\ Z \end{matrix}\right\} N,$$

may in a variety of ways assimilate several other groups of elements without forfeiting its original character. Cyaniline, melaniline† and dicyanomelaniline, and their

* A perfectly similar remark applies to a compound lately discovered by Rochleder among the products of decomposition of caffeine (Ann. Chem. und Pharm. lxxi. 7), and described by him under the name of formyline. The formula

$$C_2 H_4 N,$$

which Rochleder gives for this compound, is, after we have become acquainted with the mode in which the methyl- and ethyl-bases are produced, very improbable. There appears to me a choice only between the formulæ

$$C_2 H_3 N = \left\{\begin{matrix} H_2 \\ C_2 H \end{matrix}\right\} N \text{ and}$$

$$C_2 H_3 N = \left\{\begin{matrix} H_3 \\ C_2 H_3 \end{matrix}\right\} N.$$

The former of these formulæ is improbable, on account of the great discrepancy both in the hydrogen and platinum observed and calculated; and it may be mentioned here that the existence of a series of bases of the formula

$$C_n H_{n+1} N,$$

i. e. bases containing formyl, acetyl, propionyl (metacetyl), butyryl, &c., appears to be still doubtful on account of the electro-negative character of these radicals. By the action of bromide of acetyl, $C_4 H_3 Br$, upon ammonia, I have not as yet been able to obtain an alkaloid. The formula

$$C_2 H_5 N,$$

which is that of methylamine, discovered by M. Wurtz, has analogy in its favour. The slight deficiency in the hydrogen can, it would appear, be scarcely adduced in opposition to the formulæ. The three formulæ are represented by the following numbers, which I place in juxtaposition with the mean of the analytical results.

	$C_2 H_3 N$.	$C_2 H_4 N$.	$C_2 H_5 N$.	Mean of analysis.
Carbon	5·10	5·09	5·06	4·86
Hydrogen.....	1·70	2·12	2·53	2·45
Platinum	42·52	41·77	41·60	41·39

† It seems that the homologues of aniline yield derivatives with the same facility as aniline itself: Mr. Wilson is at present engaged in studying the action of chloride of cyanogen upon toluidine; he has obtained a beautiful alkaloid represented by the formula $C_{30} H_{17} N_3$, which corresponds to melaniline.

congeners, are well-marked instances of such increasing complexity. The constitution of the natural alkaloids may be still more intricate. However, a series of well-devised experiments will not fail to exhibit the framework of these substances, an inspection of which will enable us to reconstruct them with the same facility as we build up our series of alcohol-bases.

The powerful and defined action of bromide of ethyl which I have pointed out in this paper will, it would appear, materially assist in the solution of this problem. We might by its aid succeed in ascertaining the state of substitution in which the ammonia exists in these compounds, or in other words, whether the alkaloid in question is an amidogen-, imidogen-, or nitrile-base. Some preliminary experiments made with two natural alkaloids, with nicotine and coniine, more closely allied, it is true, with the aniline-group than quinine, &c., appear to promise a harvest of interesting results. These substances evidently contain still basic hydrogen, for on mixing them with bromide of ethyl, they are rapidly attacked, with formation of the hydrobromates of two new bases, of which the salt of the nicotine-derivative is obtained in large beautiful crystals. An extension of this study to the bases of the cinchona bark and of opium, and to the bases of the series $C_n H_{n+1} N O_4$ (glycocine, sarcosine, leucine, &c.), whose constitution is at present still very enigmatical, may perhaps lead to similar results. These substances, complicated as their construction may appear at the first glance, will perhaps be found of a surprising simplicity when subjected to a closer examination. I may here quote the curious results which various chemists have obtained by treating with nitric acid and other powerful agents several of the natural alkaloids, results from which it would almost appear that several of these alkaloids, brucine and narcotine for instance, do actually contain methyl or ethyl, inasmuch as their decomposition seems to give rise to the formation of compounds of these radicals. The presence of such radicals as methyl and ethyl in natural alkaloids, is in itself scarcely a startling fact. We are still perfectly in the dark as to whether the pyroxylic spirit which we obtain in the dry distillation of wood is actually a product of destructive distillation, or whether it pre-existed in the wood before the process. At all events we know from the splendid researches of M. Cahours on the oil of *Gaultheria procumbens*, that methyl-compounds are actually secreted in the organism of plants. Ammonia in a nascent state coming into contact with these and other compounds, might easily give rise to the formation of basic substitution-products. In a recent communication, Dr. Stenhouse* has proved that whenever ammonia separates from nitrogenous organic matter, by dry distillation, putrefaction, &c., we have invariably a formation of organic bases attending the evolution of this compound.

However, the question as to whether brucine and narcotine actually yield alcoholic compounds being still *sub judice*, it is better to defer for the present any farther speculations which might present themselves.

* Transactions of the Royal Society for 1850, Art. II. p. 56.

In conclusion, I append a synoptical view of the various basic compounds which I have derived from ammonia; this will exhibit the chief results of these researches, better perhaps than would a brief recapitulation of the several facts.

TYPE.	AMIDOGEN-BASES.	IMIDOGEN-BASES.	NITRILE-BASES.
Ammonia (Amine) $\left\{\begin{matrix}H\\H\\H\end{matrix}\right\}$ N.	Aniline (Phenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\ H_5\end{matrix}\right\}$ N.	Ethylaniline (Ethylophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.	Diethylaniline (Diethylophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.
		Methylaniline (Methylophenylamine) $\left\{\begin{matrix}H\\C_2\ H_3\\C_{12}\ H_5\end{matrix}\right\}$ N.	Methylethylaniline (Methylethylophenylamine) $\left\{\begin{matrix}C_2\ H_3\\C_4\ H_5\\C_{12}\ H_5\end{matrix}\right\}$ N.
		Amylaniline (Amylophenylamine) $\left\{\begin{matrix}H\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.	Diamylaniline (Diamylophenylamine) $\left\{\begin{matrix}C_{10}\ H_{11}\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.
			Ethylamylaniline (Ethylamylophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_{10}\ H_{11}\\C_{12}\ H_5\end{matrix}\right\}$ N.
	Chloraniline (Chlorophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}$ N.	Ethylochloraniline (Ethylochlorophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}$ N.	Diethylochloraniline (Diethylochlorophenylamine) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_{12}\begin{pmatrix}H_4\\Cl\end{pmatrix}\end{matrix}\right\}$ N.
	Bromaniline (Bromophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\Br\end{pmatrix}\end{matrix}\right\}$ N.	Ethylobromaniline (Ethylobromophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\begin{pmatrix}H_4\\Br\end{pmatrix}\end{matrix}\right\}$ N.	
	Nitraniline (Nitrophenylamine) $\left\{\begin{matrix}H\\H\\C_{12}\begin{pmatrix}H_4\\NO_4\end{pmatrix}\end{matrix}\right\}$ N.	Ethylonitraniline (Ethylonitrophenylamine) $\left\{\begin{matrix}H\\C_4\ H_5\\C_{12}\begin{pmatrix}H_4\\NO_4\end{pmatrix}\end{matrix}\right\}$ N.	
	Ethylamine (Ethylammonia) $\left\{\begin{matrix}H\\H\\C_4\ H_5\end{matrix}\right\}$ N.	Diethylamine (Diethylammonia) $\left\{\begin{matrix}H\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}$ N.	Triethylamine (Triethylammonia) $\left\{\begin{matrix}C_4\ H_5\\C_4\ H_5\\C_4\ H_5\end{matrix}\right\}$ N.

VI. *On the Development of the Great Anterior Veins in Man and Mammalia; including an Account of certain remnants of Fœtal Structure found in the Adult, a Comparative View of these Great Veins in the different Mammalia, and an Analysis of their occasional peculiarities in the Human Subject.* By JOHN MARSHALL, *F.R.C.S., late Demonstrator of Anatomy in University College, London; Assistant Surgeon to the University College Hospital. Communicated by Professor* SHARPEY, *F.R.S.*

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THE principal object of the present paper is to state the result of observations on the metamorphosis of certain of the great veins in Man and Mammalia, and on the relation between the primitive and final condition of these vessels, both when they pass through their changes in the usual order, and in cases of deviation from it.

It is well known that in the mammalian embryo the great veins entering the heart from the upper or anterior part of the body are originally symmetrical on the two sides; and that in Man, the Quadrumana and most of the higher orders of quadrupeds, the venous trunk of the left side undergoes occlusion; whilst in other Mammalia that vessel continues, and constitutes, in the adult state, a left vena cava anterior, which passes down in front of the left lung, and then along the back of the heart in the auriculo-ventricular groove to terminate in the right auricle. Certain points of analogy between these different conditions are suggested by a careful examination of the great veins in adult hearts, more especially of what is usually regarded in the human subject as the dilated termination of the great coronary vein in the right auricle. This portion of the vessel (Plate I. fig. 1, *s*), which has muscular parietes, is, on account of its width, usually named the coronary sinus. Its length may be considered as defined by a valve (*x*) placed about an inch or more from its opening into the right auricle. This valve, which was known to VIEUSSENS*, has been again recently pointed out by Dr. JOHN REID†, and is described by him as generally existing and formed of one or two segments. In all the examinations which I have made I have found it present, and always consisting of two segments; a larger one placed on the side of the auriculo-ventricular furrow, and a smaller one situated on the free side of the vein, and therefore liable to be divided in slitting up

* Traité de la Structure, &c. du Cœur. Toulouse, 1715, p. 56.

† Cyc. Anat. and Phys., Art. *Heart*, p. 597.

that vessel (see Plate I.). Into the extremity of the coronary sinus, as thus defined, the great coronary vein (*g*) may be said to open, its entrance being guarded by the valve alluded to; and along the lower border of the sinus there enter three or four venous branches (*p*, *p*, *p*), which ascend from the back of the ventricles, one of them generally forming the middle cardiac vein (*m*); the mouths of these branches are also almost invariably provided with fine valves consisting of one or two segments, but beyond the coronary sinus and the larger valve first noticed, no more valves are met with either in the trunk of the principal cardiac or coronary vein, or in any of its tributary branches.

In the hearts of the Monkey, Cat and Dog, a precisely similar arrangement is observed.

In those animals which possess a left vena cava superior, the great cardiac or coronary vein ends in that additional venous trunk, as seen, for example, in the Marsupialia, many of the Rodentia, and in the Elephant. Moreover in certain Ruminant and other animals, as for example the Sheep (Plate I. fig. 2), in which a large left azygos vein exists, arching over the root of the left lung and thence pursuing the same course to the right auricle as the left vena cava superior in the cases already alluded to, the coronary vein (*g*) opens into this azygos venous trunk (*ss'*). In both these two conditions, as I have observed in the Rabbit, Hedgehog, Ox, Sheep and Pig, the lower part of the large left venous trunk is always dilated and muscular, and at the opening of the coronary vein into it, there is found a large valve composed in some cases of one segment (*x*), and in others of two. A series of small veins (*pmp*), ascending from the back of the heart, join it at intervals between the valved entrance of the coronary vein and the opening of the venous trunk itself into the right auricle; and, lastly, the mouths of these ascending cardiac veins are for the most part regularly provided with valves, whilst, on the contrary, no valves exist along the continuation upwards of the large venous trunk, at least in the neighbourhood of the heart; nor are valves met with, as a constant condition, in any other part of the cardiac veins themselves.

On comparing, in Man and Animals, the arrangement of these vessels and the disposition of their valves, I was led to conjecture that *the dilated and somewhat muscular portion of the coronary vein, usually named the coronary sinus* (Plate I. fig. 1, *s*), together with its large and important opening (*t*) into the right auricle, as seen in Man and such of the higher Mammalia as have no left vena cava superior or left azygos vein, *was strictly analogous to the expanded lower portion* (fig. 2, *s'*) and auricular orifice (*t*) *of those additional left venous trunks*, as found in other quadrupeds; and, in fact, that it *was the persistent lower part of the left anterior primitive venous trunk*.

On this supposition, the coronary vein *proper*, in Man and the higher Mammalia, might be said to end in the so-called coronary sinus, at the valved orifice above described; and thus its mode of termination, instead of varying in different cases, would be similar throughout the entire mammalian series,—the vessel in no case reaching

the right auricle directly, but always pouring its blood, like the posterior cardiac veins generally, into a larger venous trunk.

The analogy thus indicated between the coronary sinus on the one hand, and the lower portion of the left vena cava superior or left vena azygos on the other, is apparent, not only in their likeness as to shape and structure and the disposition of their branches and valves, but also in the similarity of their situation, direction and connections with the heart, and in the resemblance, not altogether overlooked by anatomists, of their respective openings into the right auricle.

According to Rathke, however, whose authority is generally followed, the left anterior primitive venous trunk in the human subject closes and entirely disappears in the progress of development, from the root of the neck down to the heart. But if, on the contrary, the coronary sinus, as found in the adult condition, in Man and some of the higher Mammalia, be, as is above suggested, the *analogue* of, or, to express the fact in another form, be the *lower pervious portion* of the left primitive vein, might it not possibly happen that, even on the fully-formed heart, some remnant of its *upper occluded portion* should still exist, above the valved entrance of the coronary vein into the coronary sinus?

Searching, accordingly, in the adult human heart, I have found, in upwards of twenty different instances, certain parts or structures (Plate I. fig. 1, *o*, *l*, *v*) always clearly distinguishable, though varying in distinctness, which, from their position and general character, are undoubted remains of the upper portion of the left primitive venous trunk.

Analogous remnants of the left primitive vein are also to be seen, in all those Mammalia in which—as in the Dog, the Cat and the Monkey—the same amount of occlusion of that vessel occurs as in the human subject; and a comparative examination of the arrangement of the veins in different animals, of the various instances of deviation from the ordinary condition in Man*, and of the metamorphosis of these vessels in human and other embryos, has sufficed to establish, beyond a doubt, the identity of the parts under consideration.

The results of the entire investigation, together with due reference to the labours of others, may be conveniently presented under the following heads:—

1. Development of the great anterior veins.
2. Comparative view of the adult condition of these veins in Man and Mammalia.
3. Analysis of their varieties in the human subject.

* In the thirteenth observation out of twenty-four, I fortunately met with an example of double vena cava superior in the adult, a rare and interesting variety in relation to the present subject. Since then I have had presented to me a second example, occurring in a child between four and five years old. I may take the present opportunity of thanking Dr. Sharpey, Mr. Streeter and Mr. W. Bennett for aid in procuring materials for this investigation.

I. DEVELOPMENT OF THE GREAT ANTERIOR VEINS.

It has been shown by Rathke*, to whom we are chiefly indebted for our knowledge of the development of the veins, that in Man and Mammalia, as in the Vertebrata generally, the blood of nearly all parts of the embryo is returned to the heart by two pairs of venous trunks, viz. an *anterior* and a *posterior* pair, placed symmetrically in the lateral halves of the body. Besides these, however, there is a median inferior venous trunk, which forms in succession the termination of the omphalo-mesenteric and umbilical veins, and finally becomes the *vena cava inferior*.

Of the four lateral veins, the anterior pair, formed by branches from the head and neck, constitute the *jugular veins*. The posterior pair, which return the blood from the Wolffian bodies and the hinder part of the embryo, are called the *cardinal veins*. The cardinal and the jugular vein of each side join to form a short wide vessel, named the *canal of* Cuvier; and again, the two canals of Cuvier (so named from their resemblance to the ductus Cuvieri in fishes) running downwards and forwards at the sides of the œsophagus, unite in front of that tube into a common trunk, which immediately enters the yet undivided auricular portion of the heart. In the subsequent enlargement of the yet single auricle, this common trunk comes, as it were, to form part of that cavity, into which accordingly the two canals of Cuvier henceforth open separately, and thus represent two superior venæ cavæ, one on each side.

When the Wolffian bodies disappear, the cardinal veins diminish in size, returning the blood from the hinder limbs and trunk of the embryo only. In the mean time the intercostal veins are formed and united together by vertical anastomoses on each side, so as to form the azygos and hemiazygos veins. Finally, in Man, the left cardinal vein becomes, according to Rathke, *entirely obliterated*, whilst the upper portion of the vein of the right side is probably concerned in the formation of the termination of the azygos vein.

In the meantime a transverse connecting branch is developed across the lower part of the neck, between the two jugular veins. This transverse branch is rapidly enlarged, and then, in the human embryo, and also in those animals which have no permanent venous trunk on the left side, that portion of the original left jugular trunk which is situated lower down than the transverse branch, or nearer to the heart, and also the left canal of Cuvier which is continuous with it, shrink and disappear; the enlarging transverse branch across the neck forms the left innominate vein; and the lower part of the right jugular with its canal of Cuvier, receiving the remains of the right cardinal vein, now the terminal part of the vena azygos, constitutes the vena cava superior as ordinarily met with: thus the metamorphosis is complete.

In the Sheep, however, it was observed by Rathke, that the upper part of the left

* Rathke, "Ueber die früheste Form und die Entwickelung des Venensystemes beim Schafe" (Meckel's Archiv für. Anat. und Phys. 1830, p. 63); also, more particularly, "Ueber den Bau und die Entwickelung des Venensystems der Wirbelthiere"—(Dritter Bericht, über das Naturwissenschaftliche Seminar bei der Universität zu Königsberg. Königsberg, 1838).

cardinal vein and the left canal of Cuvier remain open to form the left azygos vein present in that animal; whilst that part of the left primitive venous trunk which is situated between the canal of Cuvier and the junction of the left subclavian and jugular veins, disappears, and only a subordinate twig is subsequently found in its place, which ends in a small left superior intercostal vein.

Lastly, in those animals which in the adult condition have a right and left superior vena cava, the left primitive jugular vein, together with the corresponding canal of Cuvier, remains pervious throughout life. This knowledge of the common type of formation of the veins in the Vertebrata, and of their metamorphosis in certain species by partial occlusion, suggested to Rathke the explanation of the occasional occurrence of double vena cava superior in the human subject as the result of an arrest of development. Nevertheless, the details of this metamorphosis have not been fully indicated, nor, as far as I am aware, have any persistent remnants of the fœtal structure been recognized in the adult. By Rathke himself the left primitive vein is said, in Man, to *diminish and entirely disappear from opposite the left end of the transverse vein of the neck, down to the heart*; but this seems to have been an inference from the known adult condition, and I do not know that either he or others have given any description or delineation of the development of these veins, as actually traced in the human embryo.

The metamorphosis of the primitive lateral and symmetrical venous trunks in the higher Mammalia and in Man may be said to consist of *two fundamental changes*, viz. *a*. the formation of the cross branch or communication in the neck, and, *b*. the occlusion of a greater or less portion of the left primitive venous trunk. Besides this, however, there are, during embryonic life, *c*. certain concurrent and subsequent alterations in the size, position and direction of the venous trunks which finally remain pervious. Lastly, *d*. there are the changes which take place after birth.

Development in the Sheep.

a. *Formation of the Transverse Communication in the Neck.*

In embryos measuring $\frac{1}{10}$ths of an inch, well-preserved in spirit, and in which the blood was hardened in the veins, no appearance of a cross branch was discernible. The earliest satisfactory indications of its commencement were met with in embryos from $\frac{8}{10}$ths to $\frac{9}{10}$ths of an inch in length. In these (Plate II. figs. 1, 2, 3), two little spur-shaped points, filled with hardened blood, projected towards each other from the inner borders of the jugular trunks (*a a'*) immediately above the commencing pericardium, on a level with the subdivision of the ascending aorta. In some cases, no intermediate portion of vein between these points could be detected; but in others the connection was evidently completed by a material, more opake than that around, which could be often raised as an indistinct narrow cord, containing however no

hardened blood (fig. 5, *d*). Even in embryos as long as $\frac{1}{10}$ths of an inch (fig. 4), no red line could be traced quite across the neck, although the lateral primitive veins were turgid with blood, and presented two conical projections at the situation of the cross branch.

This cross branch is supposed to be formed by the enlargement of a previously developed vessel of almost capillary dimensions, perhaps one of several such vessels passing across the neck; but it is possible that it might be formed in the same way as the other great vessels. The appearances above described would suggest the idea that this transverse branch was formed by the budding out and subsequent junction of two opposite points of the older veins, but this appearance is probably owing merely to the vessel being smaller and empty of blood in the middle of its course, or to its being accidentally broken at that point; but still it would seem that the extremities of the new transverse vein in connection with the older vessels are at first always enlarged more than the intermediate portion. In recent embryos of the Guinea Pig, measuring about half an inch in length, I have twice recognized the transverse branch as a very *minute continuous* vessel, passing quite across the neck, between the two jugular veins, just above the pericardium. In one very early embryo ($\frac{6}{10}$ths of an inch long), a small vessel, evidently a vein, traversed the neck higher up, supported by the branchial arch which was being transformed into the lower jaw; the lower cross branch was not yet formed in this case.

During the widening of the cross branch, the two jugular trunks (*aa'*) at that point gradually approach each other,—the distance between them, absolutely as well as relatively, decreasing (compare figs. 2 and 6, representing embryos of $\frac{1}{10}$ths and $\frac{1}{10}$ths of an inch in length). Instead of descending parallel with each other, these veins now incline to the middle line of the neck, opposite the cross branch, and assisted by the shortening and widening out of that vessel, they appear at length to coalesce, almost by lateral adaptation, before any diminution of the left primitive vein has begun to take place (fig. 7, embryo 1 inch $\frac{2}{10}$ths long).

In later embryos (fig. 8, 1 inch and $\frac{3}{10}$ths long; fig. 10, $1\frac{1}{3}$ inch long), in which the neck is already becoming elongated, by the time that the occlusion of the left primitive vein is accomplished, the two jugular veins, having received the large superficial veins of the neck and those from the anterior limbs, are so closely applied to each other, and their connecting branch is become so entirely absorbed into them, that they join together at a very acute angle; or rather, the vein of the left side, now the left innominate vein, runs continuously into the lower part of the right primitive vein, or superior vena cava, whilst the right innominate vein appears to fall into this large continuous trunk at an acute angle.

At still later periods, when the vertebral column projects prominently forward at the lower end of the slender neck, immediately above the narrow aperture of the thorax, this obliquity of the junction between the innominate veins is as marked as in the adult animal.

b. *Occlusion of a portion of the Left Primitive Vein.*

Before the commencement of this stage of the metamorphosis, the jugular trunks are closely approximated and open freely into each other by means of the wide and very short communicating branch (fig. 7, *d*). Previously to this change also, that portion of both primitive jugulars which is situated below the cross branch, becomes elongated in accordance with the growth of the thorax, and now, inclining outwards, descends through a much longer course upon the pericardium, beneath the pleura, to join the cardinal vein of its own side and end in the corresponding canal of Cuvier. It is just this portion of the left primitive jugular vein, viz. from the transverse branch in the neck to the commencement of the left canal of Cuvier, which becomes closed in the Sheep. In embryos measuring 1 inch and 1 line (fig. 7), the vessel (*a'*) has either not begun, or is only just beginning to shrink; but so rapidly does the process take place, that in others scarcely 1 line longer (fig. 8), the vessel is already closed, and now appears as a semitransparent cord (*o*) extending from the point of junction of the primitive jugular trunks in the neck, to the arch formed by the left cardinal vein (*b'*) and left canal of Cuvier (*c'*). This cord is finer at its lower end; it lies at first in front of the aorta, and then passes down close to the pericardium, on the left side of the ductus arteriosus; it is in contact, below, with the left pleura; the par vagum descends behind it, and it is crossed by the phrenic nerve. Close behind the upper end of this cord, but not actually connected with it, a considerable vein, formed by the left vertebral and a large perforating intercostal from the back, joins the under side of the left innominate vein.

In later embryos the above-mentioned cord becomes less and less distinct; in an embryo measuring $1\frac{1}{3}$ inch long (fig. 10) it cannot be continuously traced, and in a fœtal sheep, 4 inches in length (from the vertex to the tail), it is not perceptible. In its place, however, there is found a long ridge or elevation of the pericardium, containing fibrous tissue, which may be followed from below upwards, close to the left side of the large ductus arteriosus, in a direction towards the middle of the root of the neck. Above the pericardial sac, the traces of it are almost entirely lost.

c. *Concurrent and subsequent Changes in the Pervious Vessels.*

In *size*. As the left primitive vein is undergoing occlusion, the lower part of the right jugular vein (figs. 8, 10, *a*), and the right canal of Cuvier, simply enlarge, as Rathke states, to form the superior vena cava. The adjoining part of the right cardinal vein, having first shrunk in consequence of the wasting of the Wolffian body, remains for a considerable time as a right azygos vein, equaling in size the left azygos; but about the middle of fœtal life it is smaller than the vein on the left side, and afterwards, its connection with the right intercostal veins being gradually cut off, it slowly diminishes until it exists only as a very small vessel, or sometimes wholly disappears. The left cardinal vein (*b'*), on the contrary, forms, after the disappearance of the corresponding Wolffian body, a left vena azygos, which, though for

a time of the same size as the right azygos, afterwards surpasses it, in consequence of receiving the lower right intercostal veins, in addition to almost all those of its own side. The left canal of Cuvier (*c'*), reduced greatly in width after the occlusion of the primitive jugular vein, constitutes the intrapericardial part of the left azygos vein, and with the rest of that vessel forms a venous arch, which turns over the root of the left lung, and is connected above with the cord-like vestige of the occluded vein (*o*).

In *position* and *direction*. The cardinal veins, in order to unite with the jugular veins in the corresponding canals of Cuvier, bend forwards above the commencing lungs (figs. 1 and 2,—4, 4'), from which they are for a time separated by the upper end of the Wolffian bodies (5, 5'). The rudimentary right lung being, almost from the commencement, larger and somewhat higher up in the thorax than the left, the right cardinal vein (*b*), even at a very early period (see figs. 2 and 9), reaches higher than the vein of the left side (*b'*); a peculiarity in position which subsequently increases, so that in a fœtus of 4 inches in length the arch of the right azygos rises three lines higher up in the thorax than that of the left vein.

The cardinal veins, like the jugulars, are altogether outside the pericardium; but as soon as that sac is formed, the canals of Cuvier are found almost entirely within it. At first (figs. 1, 2, 3, *c*, *c'*) these canals pass horizontally forwards and inwards to the back of the auricular portion of the heart, into which they open on the same level, one on either side, in front of the inferior cava; but as the lungs enlarge and occupy more of the thoracic cavity, the Cuvierian canals have to descend more and more obliquely in front of the roots of those organs to reach the heart (figs. 7 to 10). In accordance with the higher position of the root of the right lung, this change in direction is more marked in the right canal of Cuvier, or future vena cava superior.

The heart itself, in the progress of growth, becomes slightly twisted, especially at its base or auricular part, its right border being turned somewhat upwards, supposing the thorax to be placed vertically (fig. 9, embryo 1 inch and 2 lines long; the parts being seen from behind). Hence the enlarged right canal of Cuvier (*c*) or upper vena cava reaches the future right auricle sooner and more directly than the smaller left canal (*c'*) or left azygos venous trunk; the former having a comparatively short and almost vertical course, whilst the latter, after having descended in front of the root of the left lung, has to turn beneath the base of the heart to gain its destined end in the right auricle. At the same time the position of the openings of the metamorphosed canals of Cuvier in the future right auricle undergo a change; for instead of both of them being placed, as at first, on the same level, one on each side of the inferior cava, the orifice of the right canal or upper cava opens widely into the highest part of the auricle, nearly in a line with the lower cava (*e*), whilst the left canal or left azygos ends at the lower and back part of the auricle close to the commencing septum. The serous layer of the pericardium is at first equally reflected over both the Cuvierian canals, but in time, whilst it covers only a smaller and smaller part of the anterior surface of the right canal, or upper cava, it forms a more and more

distinct *fold* or duplicature (fig. 10 *c'*), in which the left canal or left azygos trunk is lodged as it passes down in front of the left pulmonary vessels to reach the side of the left auricle immediately behind the appendix. Beyond that point, the vein, as it lies on the back of the left auricle, and runs along the auriculo-ventricular groove to reach the right auricle, is also covered by the serous layer of the pericardium. In the heart of a fœtus, 4 inches in length, several small veins from the substance of the left ventricle may be seen ending in the lower part of the left azygos trunk; and, amongst them, one, which joins it at an acute angle, is the future coronary vein.

d. *Changes at Birth.*

When, after birth, the short and wide ductus arteriosus shrinks, the long ridge of the pericardium with its contained fibrous tissue, already described as resting upon that vessel in the position of the occluded left vein, becomes closely applied to the left side of the aortic arch, and may be traced in the direction of a line drawn from the point of junction of the innominate veins at the root of the neck, down to the highest point of the arch of the left azygos vein.

Within the pericardium, the trunk of the left azygos occupies its proper *fold* of the serous membrane, and receives, shortly before its termination in the right auricle (as seen in Plate I. fig. 2), the coronary vein of the heart (*g*) and two posterior cardiac branches (*p*, *m*), besides a third smaller one (*p*), which might almost be said to end at once in the right auricle. The mouth (*t*) of this left azygos venous trunk is situated to the left of the orifice of the inferior cava (*e*), close to the interauricular septum, and below and behind the fossa ovalis, like that of the left superior cava in the lower Mammalia and in Birds. It has no Thebesian valve, which is represented, in the Sheep, merely by a slight ridge of the auricular parietes.

At the entrance of the coronary vein into the left azygos, there is, however, a large distinct valve (*x*), consisting of one strong segment. The two cardiac veins succeeding it are each guarded by finer valves of two segments, and the third vein generally by a single segment. Along the course of the coronary vein, there are from one to four other valves, consisting usually of one segment, but sometimes of two.

Lastly, the right azygos is now a much less important vein than that of the left side; it reaches from 3 to 5 inches higher in the chest, and is so small as to have been said by some anatomists, including Rathke, to be always wanting. Occasionally, (once in five observations) it was found to be so trivial a vessel, that it was difficult to distinguish it as the actual persistent representative of the right cardinal vein.

Development in Man.

a. *Formation of the Transverse Branch in the Neck.*

No opportunity has offered itself of observing the time and mode of origin of the transverse branch in the human embryo, though it is probably originally formed in the same way as in the Sheep and Guinea Pig. In an embryo of $\frac{17}{10}$ths of an inch in

length (Plate III. figs. 1, 2), the cross branch (*d*) was already formed. Owing to the width of the human thorax, the jugular veins do not approach each other closely at the root of the neck, as in the Sheep; the cross branch continues of a much greater length, and, at first horizontal in its direction, only assumes after a considerable time, the somewhat oblique position which it permanently holds as the left innominate vein. Rathke describes it as formed opposite the point of junction of the jugular and subclavian veins; but in the embryos dissected by myself, it is a little *lower down* than that point and immediately above the commencing pericardium.

b. *Occlusion of part of the Left Primitive Veins.*

It is not until after the transverse connecting branch is already nearly as large as either jugular vein, that the venous channels destined to be occluded begin to shrink. Previously to the commencement of this stage of the metamorphosis, the cardinal veins (figs. 1, 2, *b*, *b'*) have much diminished in size owing to the wasting of the Wolffian bodies (5); but the two halves of the venous system are still quite symmetrical, except that the arch of the right cardinal vein is higher up than the left, in accordance with the greater size and relative altitude of the corresponding lung, as already pointed out in the Sheep. From opposite the cross branch, the two jugular veins descend behind the auricular appendices outside the pericardium, to become continuous with the canals of Cuvier (*c*, *c'*), which, having received the cardinal veins, immediately enter the pericardium, and bend inwards beneath the auricular portion of the heart, into which they open, one on each side of and somewhat before the inferior cava.

In addition to a part of the left primitive jugular vein, lying outside the pericardium below the cross branch in the neck, it will be found that in the human subject, in which there is no left azygos as in the Sheep, the left cardinal vein shrinks into an insignificant branch, and entirely disappears as a distinct trunk; whilst the greater part of the left canal of Cuvier, placed within the pericardium, is also closed; its last part, however, situated on the back of the left auricle, remaining permanently open. This pervious portion of the Cuvierian canal eventually forms the coronary sinus.

The first step towards this occlusion consists in a gradual shrinking of the left primitive venous channel from the left end of the cross branch down to the back of the heart, as shown in an embryo of 1 inch and $\frac{3}{10}$ths in length (Plate III. fig. 3). The upper portion of the vein lies upon the aorta and ductus arteriosus, beneath the left pleura; whilst the lower portion, within the pericardium, crosses in front of the vessels of the left lung, lodged in a *duplicature* of the serous membrane, reminding one of the *fold* in which the left azygos vein is contained in the adult Sheep. The lower end of the vessel, placed on the back of the left auricle, is more dilated than the rest. In a more advanced embryo, 1 inch and $\frac{1}{10}$ths long, the closure was complete, and had probably been accomplished a considerable time (fig. 4). The place of the primitive vein is now seen to be occupied by a *fine cord* (*c''*), which may be followed *from the under*

side of the left innominate vein down to the back of the auricle. This cord is covered by the pleura, and crossed by the left phrenic nerve; it descends in front of the par vagum, upon the side of the aorta and ductus arteriosus to the left pulmonary artery, opposite to which it penetrates the pericardium. Within this sac it crosses the small interval between the left pulmonary artery and veins, enclosed in a minute *fold* of the serous membrane; and then, becoming applied to the back of the left auricle, expands into a small *conical pouch* (*c'*), which is narrow and pointed above, but wider below, where it opens into the right part of the yet undivided auricular cavity. No left superior intercostal vein could be found in this embryo.

In no other fœtus examined did the occlusion of the primitive left jugular vein extend quite up to the cross branch or left innominate vein; for there always remained a pervious but shrunken portion of the primitive vessel, which, as will immediately be shown, forms the *trunk* of the left superior intercostal vein. This fact is illustrated in fig. 5, *i*. In a somewhat later embryo (fig. 6), the cord of the occluded vein may be traced distinctly from the trunk of the left superior intercostal vein (*i*, which is here larger than usual), passing down through the fibrous layer of the pericardium, and entering its now narrow fold of the serous membrane (*c''*). Still later (Plate IV. fig. 9), the traces of a continuous cord above the pericardium are difficult to follow, and at the full period of fœtal life it is generally impossible to find in that situation more than a few fine vertical fibrous bands lying close beneath the pleura. The *little fold* of the pericardium, so often alluded to, soon after the closure of its contained vessel, sinks, as it were, into the interval between the left pulmonary artery and veins (Plate III. figs. 5, 6, *c''*), where it is found in all future stages, and increases in size with the other parts (Plate IV. fig. 9, *v*). Below the fold, the remnant of the closed vein descends upon the left auricle, and may be traced for a time, as a slight ridge, but afterwards, when the auricle enlarges, as an *opake line or streak*, passing close beneath the lowermost pulmonary vein, down to the apex of the *pouch-like* pervious portion of the primitive vein (Plate III. figs. 4, 5, 6; Plate IV. figs. 7, 8, 10, *c''*, and 9, *l*). By the period of birth (fig. 11), this opake streak (*l*) has usually become interrupted or obscured.

c. *Concurrent and subsequent Changes in the Pervious Vessels.*

Contemporaneously with the shutting off of the left primitive venous channels, the cross branch in the neck (Plate III. figs. 1 to 6, *d*) enlarges and, together with a short portion of the left primitive vein below the entrance of the left subclavian, forms the *left innominate* vein; a small piece of the right primitive jugular, included between the entrance of the right subclavian and the junction with the cross branch, becomes the *right vena innominata*; whilst the remainder of the right primitive jugular, below the cross branch, together with the corresponding canal of Cuvier, becomes widened and forms the *superior vena cava* (*h*). At the junction of its two constituent parts, the vena cava receives the metamorphosed right cardinal vein, now the *vena azygos*, in which the right superior intercostal vein generally ends.

The metamorphosis of the pervious vessels on the *left* side is much more complicated.

Outside the pericardium.—In one embryo already mentioned (Plate III. fig. 4), the left primitive jugular vein was converted into a cord (c''), quite up to the cross branch or left innominate vein; and in that instance no trace whatever could be detected of the left cardinal vein. In such cases as the one referred to, the left superior intercostal vein may be subsequently formed through the development of small collateral veins, or it may be entirely wanting,—its intercostal branches ending then in some other vessels. Usually, however, a piece of the left primitive jugular vein, immediately below the cross branch, remains pervious and constitutes the trunk of the *left superior intercostal vein* (fig. 5, *i*), which passes over the side of the aorta at a higher point, as the thorax becomes elongated during development. The left cardinal vein may be entirely withered, but in some cases (fig. 7) the left primitive jugular remains open from the cross branch quite down to the commencement of the canal of Cuvier, where it receives the diminished left cardinal vein (b'), thus metamorphosed into the lowest branch of an unusually large left superior intercostal vein (*i*). This vein, besides intercostal branches, may be very early found to receive thymic, pericardiac and mediastinal branches, and often a bronchial vein. In all cases, however, the left cardinal vein is effectually cut off from the occluded left canal of Cuvier (c''), and is lost or interrupted at its lower part, so that the left intercostal system becomes broken up into several streams.

Within the pericardium.—The pouch-like pervious portion of the left primitive vein, seen on the back of the left auricle (Plate III. figs. 4, 5, 6, c'; Plate IV. figs. 7, 8, *s*), is metamorphosed partly into a small *oblique auricular vein* (Plate IV. figs. 9, 10, 11, *o*), and partly into the *coronary sinus* (*s*).

On examining the back of the heart in a series of early embryos (Plate IV.)*, it will be seen, as already noticed in the Sheep, that in accordance with a certain twisting which takes place in this organ, important peculiarities in length and direction are early impressed upon the two canals of Cuvier, which are originally quite symmetrical. The right canal (figs. 1, 3, 5, *c*), or future superior cava, passes down perpendicularly from the neck, becomes widened and shortened, soon reaches the future right auricle, and enters by a wide orifice into the upper part of that cavity, nearly in a line with the inferior cava (*e*). The left canal (c'), whilst diminishing in size, pursues a more circuitous course along the left auricular cavity, beneath the base of the heart, to reach the lower and left part of the future right auricle, into which it opens by a constricted orifice surrounded by an opake well-defined border.

Even at a very early period, when this left canal of Cuvier has scarcely begun to shrink, its lower part is found, on cutting it open (figs. 2, 4), to be a *distinct vascular tube*, applied to and connected with the back of the future left auricle, but not opening into that cavity; whilst its orifice maintains its connection with the right portion of

* All the figures in this Plate, excepting fig. 11, are enlarged to two diameters.

the yet undivided auricle, and is drawn with it, in the general movement of the heart, over to the right side. This being premised, it is easy to follow the changes which the lower pervious portion of the left canal of Cuvier undergoes, after the complete occlusion of its upper part, represented now by the opake streak (fig. 9, *l*) on the wall of the left auricle, and by the minute fold of the pericardium (*v*) already described. For a time, the lower part of this canal persists as a conical pouch (Plate III. figs. 5, 6, *c'*); but subsequently (Plate IV. figs. 7, 8, from an embryo, 2½ inches long) this conical venous channel becomes elongated; its upper part forms the *oblique vein* already mentioned, whilst its lower part (*s*) pursues its course to the right along the auriculo-ventricular furrow. The coronary vein (*g*), properly so called, is now seen to end, not in the right auricle itself, but *in this venous channel*, falling into its under side at an acute angle, at a short distance from its termination in the auricle. Still later, in a fœtus 5 inches long, from vertex to coccyx, the same facts are as plainly observed (figs. 9, 10); and on cutting open the veins at this period, a *narrow oblique venous channel* (*o*), tapering to a point as it ascends to the left along the back of the auricle, may be traced from the point of entrance of the true coronary vein (*g*) upwards to the opake streak (*l*), seen on the wall of the auricle; whilst below the entrance of the coronary vein, the venous channel becomes *dilated* (*s*) as it passes to the right, receives several cardiac veins, including generally the middle cardiac, and ends in the lower part of the right auricle, close to the interauricular septum, by a somewhat contracted orifice, which is guarded by a rudimentary valve. This wider lower portion of the persistent venous channel can even now be recognized, in all respects, as the *coronary sinus*, and the valve beginning to form at its auricular orifice is the Thebesian valve. The opening of the true coronary vein into it is marked by a sharply-ridged margin, but as yet there is no valve there.

As development advances to the full period of fœtal life (fig. 11), the proper coronary vein (*g*), and the coronary sinus (*s*), become gradually more continuous in direction than heretofore, but the difference between them can be easily discerned, even externally. The muscularity of the sinus, as distinguished from the vein, becomes evident, and the opening of the latter into the former is protected by a valve, the two segments of which are for a time narrower in proportion than in the adult. Above the entrance of this vein into the sinus, a rounded recess leads upwards and to the left into the *small oblique vein* (*o*), which, taking the course of the primitive vessel, of which it is evidently the remnant, runs along the back of the left auricle, about half-way to the root of the pulmonary veins, and there ends in the opake streak (*l*) previously mentioned. This small oblique vein is crossed superficially by the muscular fibres of the left auricle; it is peculiarly straight in its course, and receives tortuous branches from the walls of the auricle.

d. *Changes which take place at Birth.*

The shrinking of the ductus arteriosus, and the simultaneous enlargement of the pulmonary artery and veins and of the left auricle, are accompanied by changes in the intrapericardial remnants of the left primitive vein. The pericardial fold is, as it were, invaded by the enlarging pulmonary vessels, and becomes relatively shorter, and more deeply concealed between the left pulmonary artery and the subjacent vein. The narrow opake streak running around the root of the pulmonary vein and along the back of the left auricle, pursues a longer course, and becomes attenuated or broken up. Lastly, as the left auricle expands, the oblique vein is less evident, and the true coronary vein and the coronary sinus become more alike to each other in direction and diameter.

Vestiges in the Adult Condition (Plate I. fig. 1, Plate V.).—The relation of the left superior intercostal vein to the primitive vessel in different cases has been already noticed. Commencing from the trunk of this vein (Plate V. *i*), there may frequently be traced a few *vertical fibrous bands* (*f*) lying beneath the pleura, posterior to the phrenic nerve, and usually accompanied by small blood-vessels and by a fine branch of the vagus nerve (13). Generally one of these bands may be actually followed to the left superior intercostal vein; and in most cases they are continued downwards through the pericardium into the pericardial fold.

This fold (Plate I. fig. 1, and Plate V. *v*), which might be named the *vestigial fold of the pericardium*, may be compared to the broad ligament of the liver, after the closure of the umbilical vein. As far as I know, it has hitherto escaped attention, though it is probably always present in the ordinary condition, as I have found it in twenty-two adult hearts*. In one instance, it could not be distinguished in consequence of complete adhesion of the pericardial surfaces, and in another, adventitious bands of membrane occupied its usual position. Sometimes it is obscured by fat, deposited within or near it. To demonstrate this vestigial fold and the opake streak continuous with it below (which are almost unavoidably injured by dividing the great vessels within the pericardial sac), the heart, great vessels and pericardium, should be removed in connection with the root of the left lung; after which, on opening the pericardium and drawing asunder the left pulmonary artery and the subjacent pulmonary vein, the fold will be seen passing nearly vertically across the deep interval between those vessels (Plate V. *v*). Besides a duplicature of the serous layer of the pericardium, including cellular and fatty tissue, the vestigial fold contains some fibrous bands, small blood-vessels and nervous filaments. Its opake well-defined and curved margin is commonly from half to three quarters of an inch in length, but I have once found it measure upwards of an inch and a half. It varies in thickness in different

* Senac states (Traité du Mouvement du Cœur, &c. Paris 1749, p. 14) that Haller, in his account of the reflections and cornua of the pericardium, following Eustachius and Lancisi, has described, amongst many others, a falciform process (*falx*) between the left pulmonary artery and veins; but I can only find in Haller a description of a "saccus" or depression between those vessels.

cases, and it may be from half an inch to an inch in depth, according to the nature of the interval between the pulmonary artery and vein. Above the pulmonary artery, the vestigial fold blends with the pericardium, and its fibrous bundles may frequently be traced into those already described as passing beneath the pleura up to the left superior intercostal vein. Its lower end is lost on the side of the left auricle in the *narrow opake* and often interrupted *streak* (*l*), which courses around the root of the lower left pulmonary vein. This streak represents the part of the left Cuvierian canal which has undergone the greatest amount of obliteration, and it is sometimes almost entirely wanting. In the same situation scattered whitish bands are commonly seen beneath the serous membrane of the back of the left auricle, closely connected with the muscular fibres and descending towards the oblique vein: amongst them there are some fine branches of nerves. They mark only the *track* of the previously existing vein. In some instances a prominent ridge exists in their place upon the back of the auricle.

The *small oblique auricular vein* (*o*), which has been shown to form part of the pervious portion of the left canal of Cuvier, is remarkably constant; and indeed has been recognized by some of the early anatomists as a branch of the great coronary vein*. This short vessel is readily distinguishable from its tributary branches by its direct course, a character not possessed by the cardiac veins generally. Moreover, it is as it were imbedded in the walls of the left auricle, so that it appears covered by muscular bundles, like the coronary sinus itself. Frequently it measures from half an inch to an inch in length, and sometimes is as large as a crow-quill, but more commonly it is smaller, and will admit only the head of a pin. I have once seen it an inch and a quarter in length, and as wide as a common goose-quill; but, however large it may be, its opening into the coronary sinus is never provided with a valve. Its upper end either tapers and ends in a fine branch; or, as more frequently found, especially in young subjects, it does not alter much in width as it ascends, but terminates rather abruptly, and receives, close to its extremity, one or two tortuous lateral branches of nearly equal size.

In some instances I have found a long slender vessel ascending from the upper part of this short vein, along the back of the auricle into the vestigial fold, and ultimately through the pericardium, just above the root of the left lung. It there joins

* It is represented by Ruysch (Thesaur. iv. tab. 3. fig. 1), and also by Senac (*op. cit.* planche 2). Haller (Oper. Minora, t. i. lib. i. p. 11) speaks of one particular branch of the great coronary vein coming from the left auricle. Theile (Sommerring's Anatomy) has a similar statement. This small vein has also been occasionally indicated in drawings of the heart given for other purposes; and it may be seen readily in most injected hearts preserved in anatomical museums.

Vieussens (Traité du Cœur, pp. 2, 55, planche 1. fig. 2, and planche 5. fig. 2) mentions and represents in two instances, as if ordinarily present, a large branch of the coronary vein in the situation of this oblique vessel, which he describes as returning the blood from the pericardial sac. Haller remarks (Op. Min., t. i. lib. i. p. 11, note) that he has never seen this *vein of the pericardium*, which is certainly represented by Vieussens, both longer and wider, than, according to my experience, the oblique vein ever is in the *human* heart.

a small branch descending from one of the veins accompanying the phrenic nerve, and so is connected with the left superior intercostal vein. This slender vessel, which receives many little branches along its course, is not however part of the metamorphosed left primitive vein, but is formed by the enlargement of the minute inosculating veins of the parts which occupy the position of the obliterated vessel. In one case indeed, which was carefully dissected, the lower end of this small vein was found not to coincide with the trunk of the oblique auricular vein, but to fall into one of the lateral tortuous branches of that persistent vessel.

The arrangement of the valves in the *coronary sinus* in the adult has been fully described in the introduction to this paper. The abrupt commencement of the sinus, pointed out by Dr. J. Reid, is owing to a rounded recess, formed on the auricular side of the principal valve (Plate I. fig. 1, *x*), into which the unvalved orifice of the short oblique vein (*o*) is *constantly* found to open. The sinus itself is described by the same observer as having "the appearance of a muscular reservoir placed at the termination of the (coronary) vein, similar to the auricles (auricle?) at the termination of the two cavæ;" but its relations to the left primitive vein in the embryo, and its analogies in the lower animals, have not hitherto been mentioned by anatomical writers; though Professor Sharpey has been accustomed to point out, in his lectures, the resemblance between the coronary sinus and the lower end of the left superior cava.

II. COMPARATIVE VIEW OF THE GREAT ANTERIOR VEINS IN MAN AND MAMMALIA.

Our knowledge of these veins in most of the Mammalia is still deficient, and many of the descriptions which exist are incomplete in points of detail. To the information gathered from other sources, I may add the results of observations made by myself on the veins of the Hedgehog, Rabbit, Rat, Mouse and Bat; of the common Mole, the Sheep, Ox, Hog, Guinea Pig and Horse; and of the Polecat, the Seal, the Dog, the Cat and the Monkey*.

* Since the observations and deductions contained in this paper were completed, and the paper itself entirely written, I have seen in the 4th and 5th No. of Müller's Archiv for 1848, a short but very interesting communication by Dr. Bardeleben of Giessen, entitled "Ueber vena azygos, hemi-azygos und coronaria cordis bei Säugethieren," in which, after classifying the different Mammalia according to the condition of the *Azygos* and *Hemi-azygos* veins, as observed by Rathke (*op. cit.* 1838) and himself, into four groups,—viz. I. those having neither of these veins; II. those having both; III. those having an azygos only; and IV. those having a hemiazygos only,—he arrives, from a comparison of the adult condition of the veins in the different cases, at the same conclusion as myself in regard to the analogy of the coronary sinus with the lower part of the left vena azygos or left vena cava superior. "If," he says, "the left canal of Cuvier continues in connection with the left jugular vein, so as subsequently to form the left vena cava superior, the coronary vein is said to open into the left superior cava. If all the blood is conveyed across the neck by the anastomosing branch between the left and the right jugular veins, and the portion of the left jugular between this cross branch and the left canal of Cuvier disappears, the last-named vessel continues to be connected with the intercostal system only; and then the coronary vein may be said to end in the left or hemi-azygos, or *vice versâ*. Finally, this connection of the left canal of Cuvier being also obliterated, there remains only that portion of the vessel in which

All the varieties of arrangement hitherto observed in the great anterior veins of the Mammalia may be classified according to the amount of deviation which they present from the type, pointed out by Rathke, as originally common to all the Vertebrata, viz. that of four lateral primitive trunks.

The modifications of this type observed in the cold-blooded Vertebrata are strictly of a subordinate kind, affecting merely the relative size which particular vessels ultimately acquire. Even in birds there is no fundamental deviation from the original type. The four primitive lateral veins persist. No transverse branch is formed across the root of the neck, though a free communication exists between the jugular veins just beneath the skull. The right and left superior cavæ remain independent of each other as originally laid down, and each receives its own azygos vein.

Amongst the Mammalia, however, there appears to be no instance in which some change from the common primitive type does not take place. Throughout the whole class, so far as is known, there is the addition of a communicating branch across the root of the neck, between the two anterior primitive venous trunks. It is found even in the low bird-like Monotremes; and, should it prove to be universal, it will constitute one characteristic mark of the mammalian venous system.

The formation of this transverse communicating branch, which of necessity *precedes* the occlusion of the left primitive vein in the higher mammalian embryo, appears as the first, the simplest and the only change in the lowest forms of the mammalian series. Superadded to this preliminary step in the fœtal development, and superadded also in the highest forms of adult Mammalia and in Man, is found another change, depending on one of two modes of partial occlusion of the left anterior primitive venous trunk.

In this way *three* different permanent conditions arise. In all of them the transverse communication in the neck exists. The right venous trunk always constitutes the vena cava superior of that side; but the left vein either forms,—A, a similar large venous trunk on that side, named a left vena cava superior, which receives the left jugular and subclavian veins, the left intercostals and certain cardiac veins; or B, it is reduced to a smaller left venous trunk, which receives merely the left intercostal veins and some cardiac veins; or, C, it remains as a still smaller vessel, receiving only a few cardiac veins from the substance of the heart. These three conditions accordingly are distinguished by severally presenting—

A. A right and a left vena cava superior.

B. A right vena cava superior and a left azygos venous trunk.

C. A right vena cava superior and a left cardiac venous trunk or coronary sinus.

the veins from the substance of the heart terminate, and which will then be recognized as the great coronary vein. This is the condition in Man and in most Mammalia. In fact, in no mammalian does the left canal of Cuvier entirely disappear. Even in cases where by far the largest portion of it is obliterated, that part which runs along the posterior transverse furrow of the heart remains as the trunk of the cardiac veins." I have availed myself of Dr. Bardeleben's memoir, to introduce some additional examples of varieties of the great veins in animals.

Group A. *A right and a left vena cava superior.*—This condition exists in a large number of the lower Mammalia, viz. in the Monotremata* and Marsupialia†; in most Rodentia, as in the Dormouse*, Marmotte*, Rat‡§, Echimys*, Mouse‡§, Squirrel*‡, Beaver*, Hamster*, Mole of the Cape*, Hare‡ and Rabbit*§‡. It is found also in the Elephant*‖ amongst Pachydermata; and in the Hedgehog‡§ and Bat*‡§ amongst Insectivora and Cheiroptera.

In all such cases, the cross branch in the neck, when sought for, has been found. The left vena cava superior always descends in front of the root of the left lung, and then turns beneath the base of the heart, and after receiving the great coronary and other cardiac veins in its course, opens into the right auricle¶.

Owing to *subordinate* modifications in the azygos veins, this group may be again subdivided as follows:—

a. An azygos vein on each side.
  a. Of equal size.
    Ex. Monotremes. Marsupials (?).
  b. Of unequal size.
    α. Left azygos the larger.
      Ex. Hedgehog**, Rat, Mouse**.
    β. Right azygos the larger.
      Ex. Rabbit.

b. An azygos vein on one side only.
  a. A left azygos only.
    Ex. (?).
  b. A right azygos only.
    Ex. The Squirrel. The Hare. The Rabbit is a near approach to this condition, the left azygos being very insignificant.

c. Azygos vein wanting (?).

Group B. *A right vena cava superior and a left azygos venous trunk.*—This arrangement prevails in most of the larger quadrupeds. It occurs in the Ungulates, Rumi-

* Meckel (Anat. Comp. par Jourdan, t. ix.) is the authority for including these animals.

† Meckel. Also Owen (Cycl. Anat. and Phys.).

‡ Rathke (Dritter Bericht, &c. Königsberg, 1838).

§ The Author. ‖ Mus. Anat. of University Coll. and of Royal Coll. of Surg. London.

¶ In the Marsupialia, and also in the Monotremata, the left upper cava joins the inferior cava just before that vein expands into the right auricle (Owen, Articles *Marsup.* and *Monotrem.* Cycl. Anat. and Phys., vol. iii. pp. 307, 309 and 390). This peculiarity, which is particularly marked in those marsupials which have a large vena cava inferior (owing to the size of their hinder limbs), appears to be due merely to an opening out, as it were, of the orifices of the two veins, so that they meet and blend with each other.

** Eustachius (Opuscula Anat. de venâ sine pari, p. 273) describes the large left azygos of the Hedgehog and Mouse, and also a splitting of the inferior cava, in the former animal, into two branches, of which one is evidently the left upper cava.

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nants and Solipeds, as illustrated in the Hog*†, Wild Boar and Guinea Pig†; in the Sheep*†, Goat*‡, Ox*†, Dicotyles‡ and Moschus javensis‡, and in the Horse†. It is also present in the common Mole†.

The cross branch in the neck is necessarily present and forms the left innominate vein. The left azygos trunk arching over the root of the corresponding lung, descends in front of it and then turns (like the left vena cava superior in the former group) beneath the base of the heart to reach the right auricle, being first joined by the great coronary and some other cardiac veins.

Several gradations in the size of this left azygos trunk are met with in this group, which further observation on recent animals would probably render more complete, and which conduct by degrees to the third group, where the left venous trunk, reduced to its smallest persistent remnant, receives only veins from the substance of the heart.

Thus in the Hog, the left azygos trunk is very large, and returns the blood not only from its own side, but from the lowermost intercostal spaces of the right side also§. In the Sheep and Ox it is, comparatively speaking, smaller. Finally, in the Horse, it is reduced to a very fine vessel, so that the left venous trunk conveys scarcely more than the blood from the cardiac veins; and in one case I found it quite closed as it passed along the left auricle‖.

This gradual diminution of the left azygos trunk is accompanied by an equivalent increase in the size of the right azygos vein. For example: the right azygos is small and sometimes even wanting in the Hog; it is always an insignificant branch in the Sheep; it is very evident in the Ox; and very large in the Horse. In the last-named animal it returns most of the blood from the left intercostal spaces also, and thus exhibits the reverse of the condition observed in the Hog; and approaches, in this respect, the characters of the third and last group¶.

* Eustachius (*op. cit.* p. 273) describes the left azygos in the Ox, Goat, Sheep and Hog, as passing over the left bronchus, and states that the coronary vein ends in it. Bartholine, Thom. (Hist. Anat. 84. Cent. ii. p. 322) appears to have seen the left azygos in the heart of a lamb. Lancisi (Epist. de venâ sine pari, Morgagni's Advers. Anat. V. p. 80) mentions the left vena azygos in the same animals as named by Eustachius. Ridley (Observat. Medic. Pract. p. 219. In vitulo) says that, in the Sheep and Calf, the azygos is a *left* vein, which he imagined emptied itself into the left auricle or left pulmonary vein. Scarpa (Tabulæ Neurolog. tab. 7. fig. 4) mentions and also figures the left azygos vein in the Calf "ending in the trunk of the coronary vein."

† The Author. ‡ Bardeleben.

§ Correctly described by Lancisi (*op. cit.* p. 80).

‖ It is said by Rathke to be absent in the Horse; and by Bardeleben in the Ass.

¶ The transition from this to the third group is exemplified not only in the Horse and Ass, among Solipeds, but also in the Ruminantia; for I find that in the injected heart of the Camel (Museum of the Royal Coll. of Surgeons, London, Preparations 111, 112), the only trace of a left azygos visible consists apparently of a rather large oblique branch of the coronary vein on the back of the left auricle. The injected heart of the Tapir (Mus. Royal Coll. Surgeons, Preparation 105), in which animal Bardeleben says the left azygos is wanting, also exhibits a similar condition, the oblique vein being so large that it may be a rudimentary left azygos vein.

Group C. *A right vena cava superior, and a left cardiac venous trunk or coronary sinus.*—This arrangement prevails in the higher Mammalia, as in the Whale*, Dolphin* and Porpoise* among Cetacea, in the Seal†, Walrus*, Dog†, Cat†, Tiger‡, Hyæna‡, Polecat† and Ermine‡ among Carnivora, in the Quadrumana, as for example, in two small species of Monkey†; and lastly, in the human subject.

The left primitive trunk, now reduced to a cardiac vein, forms the *coronary sinus, with its small oblique branch* on the back of the left auricle, and having received the great coronary and some other cardiac veins, opens into the right auricle. The oblique vein is more or less evident in different cases. Thus it is large in the human subject; very apparent in the Dolphin, smaller in the Porpoise and the Dog, less evident in the Whale and Walrus, and very small in the Seal, Cat and Tiger§. The *vestigial fold* is more distinct in Man than in any animal which I have hitherto examined in the recent state; but it is readily seen in the Monkey, Dog and Cat.

Almost invariably the right azygos persists, whilst the lower intercostal veins of the left side, instead of forming a left azygos venous trunk, unite into an azygos minor which joins the right azygos. Variations in the extent of the azygos and azygos minor constitute subordinate peculiarities. In the Cetacea‖, the remarkable condition is found of total absence of the right azygos as well as of the left azygos vein.

Peculiarities of the coronary vein and sinus in certain animals.—In the Ornithorhynchus, in which animal the left superior cava joins the inferior cava immediately before its termination in the right auricle, the coronary vein is said to open directly into the auricle by a separate orifice *to the right* of the inferior cava¶. It seems not improbable that in this case the vein in question is rather a *posterior cardiac* vein, ascending upon the back of the ventricles, the vessel in the ordinary position of the coronary vein being diminished in size or absent. In very small animals having a left anterior venous trunk, as in the Mouse and Bat, I have observed that this condition exists**.

The arrangement of the valves of the coronary and other cardiac veins at their respective terminations in the coronary sinus, the left azygos trunk or the left vena cava superior, has already been examined and compared (pp. 133, 134). As to the Thebesian valve, it is present in every instance in which the left venous trunk forms

* Preparations in Mus. Royal Coll. Surg. Lond.: Whale, No. 135; Dolphin, No. 127; Porpoise, No. 130; Walrus, No. 76; Tiger, No. 68: also Mus. University Coll. Lond.

† The Author. ‡ Bardeleben.

§ Some of these observations have been made only on dried injected hearts.

‖ Von Baer (Nova Acta Acad. Cæs. Leop. Carol. vol. xvii. p. 408), also heart of the Whale, Mus. Royal Coll. Surg. Lond. Prep. No. 135.

¶ Meckel (quoted in Prof. Owen's Art. *Monotremata*, Cycl. Anat. and Phys. p. 390).

** It is also seen in the small heart of the common fowl, though in the larger heart of the Ostrich the coronary vein occupies its usual position and opens into the left superior cava (Owen, Art. *Aves*, Cycl. Anat. and Phys. vol. i. p. 330).

a coronary sinus receiving veins from the heart alone, as in Man, and in the Monkey, Dog and Cat: but amongst those animals which have a left azygos or left superior cava, it is certainly absent, as in the Calf, Hog, Sheep, Horse, Ass*, Rabbit and Hedgehog.

III. ANALYSIS OF THE VARIETIES OF THE GREAT ANTERIOR VEINS IN MAN.

The different conditions of the great anterior veins in the Mammalia having been classified according to their progressively increasing deviation from the common vertebrate type, an attempt may be made, in analysing the varieties of these vessels met with in Man, to retrace the series from forms presenting the most complex metamorphosis to such as manifest no fundamental change whatever. In this series the ordinary condition of the veins is included as the *most frequent* actual variety.

The formation of the cross branch at the root of the neck being regarded as the initial step in the metamorphosis of this portion of the human as of the mammalian venous system, the varieties of these veins in Man may be divided into two classes, according to the *presence* or *absence* of this transverse branch.

The occurrence, in one or another degree, or the entire failure of the subsequent stage of the metamorphosis, viz. the occlusion of one of the lateral primitive veins, suffices to distinguish the *first* class of varieties into three groups, corresponding with those already indicated as the regular conditions in different Mammalia. A. In the first group, comprehending the normal condition, in which the occlusion is of the greatest known extent†, the persistent portion of the vein, after metamorphosis, conveys only the blood from the substance of the heart, and forms a *cardiac venous trunk*. B. In the second, it would also return the blood from its own side of the thorax, and thus constitute an *azygos venous trunk*. C. In the third, where no occlusion occurs, it transmits the blood from the whole of its own side of the upper part of the body, and is then a *second vena cava superior*.

In all of these cases, one of the lateral primitive veins is developed into the ordinary vena cava superior, and in most instances this is the vein of the right side, whilst that of the left undergoes metamorphosis; but the reverse of this may happen, as

* Reid (Art. *Heart*, Cycl. Anat. and Phys. p. 397).

† It has already been shown that *complete* occlusion of this primitive vein (*i. e.* from the neck down to its entrance in the right auricle) does not (as Rathke supposed) occur, in the ordinary condition, even of the highest Mammalia or of Man, nor has it yet been seen as an occasional variety. That it ever does happen is scarcely probable; for just as in the utmost known amount of abnormal obliteration of the inferior cava, the hepatic veins always concur to form a short inferior trunk, which opens into the right auricle, so the confluence of the coronary and other cardiac veins may set a like limit to the occlusion of the left anterior primitive venous trunk. Nevertheless, it is possible that the process might extend to the closure of its lower end or coronary sinus also, the blood from the substance of the heart then returning to the right auricle directly through enlarged anterior or posterior cardiac veins, or taking some altogether different course. In a curious case recorded by Le Cat, and hereafter to be particularly mentioned, the auricular end of the left primitive vein seems really to have been closed, though its channel continued pervious up to the neck.

when the viscera are transposed; so that *transposition*, as an additional cause of peculiarity, may affect any of the preceding groups.

Lastly, the three principal groups may present subordinate variations, depending on peculiarities either in the upper vena cava itself, or in the azygos veins, or in the coronary vein of the heart.

In the *second* class of varieties, in which no cross branch is formed in the neck, both of the lateral primitive veins are necessarily persistent, each carrying back the blood of its own side. Such cases may also present peculiarities in the azygos system, or may be complicated by transposition of the heart.

Though the records of the varieties in these great veins in the human subject do not as yet supply examples of every conceivable deviation, and though the descriptions of many are somewhat obscure or incomplete, they appear to admit of arrangement according to the scheme just mentioned.

CLASS I. TRANSVERSE BRANCH IN THE NECK, PRESENT.

Group A. *The second anterior venous trunk reduced to a cardiac venous trunk.*

a. *Without transposition.* A *right vena cava superior, and a left cardiac venous trunk or coronary sinus.*—This is the ordinary condition of the great anterior veins. It is accompanied by numberless subordinate modifications, occurring either in the right superior cava itself, or in the azygos systems, or in the coronary vein of the heart, and includes by far the greater number of the recorded varieties of these veins.

a. *Varieties in the Right Superior Vena Cava.*

These appear to be very rare. A presumed example is recorded by Rosenthal*, in which, the auricles and ventricles being undivided, two superior veins, called two superior cavæ, joined immediately before ending in the single auricle, into which however they opened by separate mouths. In this case the upper cava may have been shorter than usual, so that the two superior veins were the venæ innominatæ; but the description is not sufficiently full†.

b. *Varieties in the Right and Left Azygos Systems.*

These are exceedingly numerous, and require to be referred to several heads:—

1. *The right intercostal system consolidated, the left intercostal system broken up.*—In this, the most frequent arrangement, the right intercostal veins end principally in the azygos vein, but partly also in a right superior intercostal vein. The left inter-

* Abhandl. aus dem Gebiete der Anat. Physiol. und Pathol. Berlin, 1824, p. 150.

† It may be here mentioned that Wrese (De Ectopia Cordis, &c. 1818, Berolin. sect. 37, 48) has twice found the left innominate vein (the primitive cross branch) in malformed fœtuses, passing across the neck behind the trachea and œsophagus.

costal system loses its integrity as development goes on; its middle and lower portions end in the azygos vein, either through an azygos minor, as in the usual case, or if that vessel be wanting, by independent intercostal branches*, or by both of these ways together†; or its lower branches may descend to the lumbar or renal veins†. Its upper portion forms a left superior intercostal vein.

The azygos vein, in these cases, formed towards its termination by the persistent trunk of the right cardinal vein, usually ends in the upper vena cava (the right canal of Cuvier), but its place of termination is said, though very rarely, to be moved on, as if by the fusion of the canal of Cuvier with the right auricle, so that it may end in the auricle itself‡, or even approach the neighbourhood of the inferior cava, within the pericardium§(?), as occurs in some animals.

The right superior intercostal vein, which is not formed by any part of the primitive venous trunks, frequently joins the arch of the vena azygos itself‖; but, without any other coexistent variation, its place of opening may be removed to the upper vena cava‖, to the right innominate‖, or subclavian veins¶, or even to the vertebral vein**.

The left superior intercostal vein, the trunk of which is generally formed by the metamorphosed portion of the primitive left jugular vein, immediately below the transverse branch in the neck, is, when present, almost constant in its mode of termination, ending at the underside of the commencement of the left innominate vein††.

2. *The right intercostal system retaining its integrity, but unusually large.*—There are various degrees of this condition, in which the azygos vein, besides receiving all the intercostal branches of its own side, including the superior intercostals, is joined by more than usual, or even by all the separate branches of the left side‡‡. In this latter case the ordinary left superior intercostal vein is very small or wanting, the left primitive jugular trunk having become obliterated quite up to the cross branch in the neck, as exemplified in the embryo, Plate III. fig. 4.

A still more remarkable enlargement of the azygos vein has been rather often met with, in those cases in which, the inferior cava being deficient, the azygos conveys all the blood usually brought back by that vessel excepting what returns from the liver, which continues to pass by a short hepatic venous trunk directly into the heart. The

* Sömmerring (De Corporis Humani Fabricâ, vol. v. p. 373).

† Breschet (Recherches sur le Système Veineux. Note, p. 8–10).

‡ Cheselden (Philosophical Transactions, 1713, vol. xxviii. p. 282). There is a doubt about this case, which is again noticed in p. 161. Breschet (*op. cit.* p. 9. note) in a child ten to twelve years of age. Sömmerring (*op. cit.* p. 372).

§ Sömmerring (*op. cit.* p. 376).

‖ Breschet (*op. cit.* p. 12).

¶ Hildebrandt (Lehrbuch der Anat. des Menschen, 1803, vol. iv. p. 281).

** Haller (Element. Physiol. t. iii. p. 107; also t. i. lib. iv. pp. 308, 320).

†† Hildebrandt (*l. c.*).

‡‡ Breschet (*l. c.*; also pl. 1. livr. i.).

course of the lower part of this devious vein may vary; but above, it may always be identified as the enlarged azygos (originally the right cardinal vein*).

3. *The trunks of the right and left intercostal systems nearly equal.*—The several modifications of this condition constitute the different varieties of so-called *double vena azygos*; but although the azygos minor or hemi-azygos is in all these cases much enlarged by consolidation of its parts, yet it must be carefully discriminated from that true form of left vena azygos which exists, for example, in the Sheep, and in some animals having a left vena cava superior.

α. In one set of these cases, the size and termination of the azygos vein itself being as usual, the azygos minor, enlarged and extending higher than ordinary, crosses over to the right side and joins the azygos vein near to or at its termination in the superior cava†, or ends in the upper cava itself‡, or even it has been said in the right auricle§. Most frequently, the azygos vein ending as usual, the enlarged azygos minor or left azygos, as it is often called, ascends on its own side and ends in the place of the left superior intercostal vein in the left vena innominata, as if by persistent connection of the left cardinal vein, with the short part of the left primitive jugular below the cross branch in the neck‖.

* 1. Winslow (Exposition Anatomique, &c. t. iii. pp. 119 and 157). This example, which is clearly described, seems to have been overlooked.

2. Abernethy (Philosophical Transactions, 1793, p. 69). The preparation is figured in Prof. Quain's Anatomy of the Arteries, pl. 5. fig. 5. The aorta arches over the right bronchus as well as the vena azygos.

3. Wistar (A System of Anatomy, &c. Philadelphia, 1811–14, vol. ii. p. 320). This was originally regarded as an example of *absence* of the azygos vein, the enlarged vessel being considered as the inferior cava, rising higher up than usual, and ending in the vena cava superior. It is so quoted by Gurlt (*ut infra*). The specimen was found in 1813, and afterwards given by Wistar to Dr. Horner, by whom it has been correctly described and explained in the Journal of the Academy of Natural Sciences of Philadelphia, 1818, vol. i. part ii. p. 407 (with a plate). Otto (Lehrbuch der Anat. Patholog. p. 348, note 30) has been thus led to reckon it as two separate cases.

4. Jeffray. This preparation, mentioned by Otto (*op. cit.* p. 348) as having been seen by him in the collection of Prof. Jeffray, is, as I am informed by Prof. Allen Thomson, now in the Museum at Glasgow.

5. Otto himself (*loc. cit.* and seltene Beobacht. p. 67) met with an instance, which was afterwards fully described and represented by Gurlt (De Venar. Deformitatibus, &c., 1819, p. 20).

6. Weber (Rust's Magaz. &c. vol. xiv. p. 536).

† Haller (*op. cit.* t. iii. p. 107), Winslow (*op. cit.* p. 121), Sandifort, three cases (Observ. Anat. Path. lib. ii. c. vii. p. 126, and lib. iv. p. 12).

‡ Blasius (Observat. Anatom. p. 116; also Observ. Medic. p. 53. tab. 7. fig. ii. 1711). Sandifort (*op. cit.* lib. iv. p. 98).

§ Sylvius, Jacobus (Opera Medica, Geneva, 1635. p. 144). In the body of Antonius Massa, Chirurgus, two azygos veins were found, "unam ab aure dextrâ, alteram inferiorem a cavâ cordi adapertâ." It is assumed by Eustachius (Opuscula, &c. p. 274) that this was an example of double azygos, one left and the other right, but the brevity and obscurity of the original account render it impossible to decide on its true nature.

‖ Most of the cases recorded as examples of "double vena azygos" are of this kind. See Eustachius (Opuscula Anat. p. 274; and Explicat. Tab. Anat. by Albinus, tab. 4. figs. i. ii. iii.). Lancisi (De Venâ sine pari, in Morgagni's Advers. Anat. V. pp. 82, 87, 94). Winslow (Expos. Anatom. T. III. p. 121).

β. A variety of double vena azygos is described by Bartholine, which may have been owing to the azygos and azygos minor, of nearly equal size, ending in the corresponding superior intercostal veins*.

γ. In other kinds of double azygos, a right and a left vein coexist, and becoming widened below, discharge themselves in the lumbar or emulgent veins†.

4. *The right intercostal system broken up, the left more consolidated.*—In this somewhat rare condition, the trunk of the azygos vein is reduced to a very small vessel, ending as usual in the superior cava; but most of the right intercostal veins pass over to the left side, where they form a large left azygos ending above in the left innominate vein through the left superior intercostal‡.

5. *The right azygos vein entirely wanting.*—In all the preceding varieties of the intercostal system of veins, with their intermediate gradations (excepting β), the vena azygos is still present, though sometimes represented by a very small vessel. The persistence of the right cardinal vein is therefore remarkably constant. It is possible, however, to conceive this vessel to be entirely obliterated, so that there should be no vein arching over the right bronchus to end in the upper cava. No perfectly unexceptionable example of this condition has been recorded§.

c. *Varieties in the Coronary Vein of the Heart.*

As might almost be anticipated, these are few and very rarely occur. One instance is mentioned by Meckel and one by Jeffray in which the coronary vein ends in the left auricle‖. The most unexpected deviation, however, is that in which the blood of the coronary vein reaches the heart through some remote vein instead of

Mascagni (Syst. Vas. Lymphat. tab. 19). Haller (Element. Phys. t. iii. sect. i. p. 107). Otto (*op. cit.* pp. 347, 348, notes 18, 20). Wrisberg (De Venâ Azygâ duplici, &c. 1778. Observat. 1 and 2). Wilde (Comment. Petropol. vol. xii. p. 318). Breschet (*loc. cit.* p. 9). Lauth (Manuel d'Anatomiste. Paris, 1826, p. 592); and several other authors.

* Bartholine, Thom. (Hist. Anatom. 84. Cent. ii. p. 322. 1641). "I have often seen," he says, "in man and animals a double vena azygos, one on each side, leading from the axillary veins."

† Eustachius (Explic. Tab. Anat. xxvi. xxvii.). Breschet (*loc. cit.*).

‡ Valentin (Journal de Médecine. Paris, 1791, tom. 86, p. 238).

§ One is related by Wrisberg (*op. cit.* Observat. 3), which, he remarks, was unique in 200 observations; but it seems probable that the vein was here obliterated by the effects of pressure. There was no azygos ending in the upper cava, but all the blood from the right side passed into the left vein, which was very large, and joined the left subclavian opposite to the termination of the thoracic duct. The subject was a boy, aged five years. The right lung was changed into a solid substance (steatoma), and it was universally and firmly adherent. Large hardened bronchial glands were found along the right side of the trachea down to the bronchus. On the left side the lung was free.

‖ Meckel (Handbuch der Mensch. Anat. vol. iii. p. 67). The case is also described by Lindner (Diss. de Lymph. Syst. Halæ, 1787, p. 21). Jeffray (Observat. on the Heart of the Fœtus, p. 2). The preparation which exhibits this very remarkable deviation, is now in the Museum of the University of Glasgow, and has recently been carefully re-examined by Professor Allen Thomson and Professor Sharpey.

through the coronary sinus. Le Cat* has recorded the following interesting variety, occurring in a child eight days old, in which he found "les veines coronaires réunies dans un seul tronc, qui sans pénétrer dans l'oreillette droite, se jettoit dans la veine souclavière gauche." The course pursued by this *single trunk* from the heart to the left subclavian vein is not described; and, anomalous as this remarkable case has hitherto appeared, it is, perhaps, an example of the closure of the orifice of the left primitive vein in the right auricle, accompanied by a pervious condition of that vessel up to the cross branch in the neck.

When the posterior cardiac vein is large and ends directly in the right auricle†, the great coronary vein and coronary sinus may be comparatively small, but instances of its extreme diminution, or entire absence, only occur with some other deviation‡.

b. *With transposition. The vena cava superior on the left side, and a coronary sinus on the right side.*—When the arch of the aorta passes over the right bronchus, the veins do not always suffer transposition also, for in those cases in which the aorta regains the left side of the vertebral column as it descends, the vena cava superior, together with the azygos, continues on the right side§. But in complete transposition of the viscera (including the heart and great arteries), the vena cava superior descends on the left side, and the azygos vein is transposed to that side also‖. Here, the metamorphosis by occlusion has affected the right primitive veins, instead of the left; and, the heart itself being entirely transposed, it is presumable that there would be found, in a recent specimen, a right cardiac venous trunk, that is to say, a coronary sinus on the right side, receiving the great coronary vein, together with an oblique auricular vein, a *vestigial fold* and the other remnants of the occluded second primitive venous trunk, as in the usual case.

* Mémoires de l'Acad. des Sciences, 1738, Hist. p. 44. This is a case already referred to in the note to p. 153. Dr. John Reid (Cyclop. Anat. and Phys. Article *Heart*, p. 597) has suggested that Sœmmerring had Le Cat's case in view, when he states (De Corp. Humani Fabr. vol. v. p. 340) "rarissime vena hæc in venâ subclaviâ *dextrâ* finitur," being probably misled by an inadvertence of Haller, who, in quoting the case, has substituted the word "*dextram*" for "*sinistram*" (Elem. Physiol. t. i. p. 375, editio 1757). It may be added, that the termination of the coronary vein in the *left* subclavian is, as explained in the text, readily reconcileable with the mode of development.

† Otto (*op. cit.* p. 347, n. 8) and other authors.

‡ In one instance recorded by Lemaire (Bull. des Scienc. Med. 1808, vol. v. p. 21), two coronary veins are said to have joined a pulmonary vein, and so reached the right auricle; but the facts seem to bear another explanation, the *pulmonary vein* in question being apparently a *left superior cava* descending in its wonted circuitous course beneath the root of the left lung, and receiving two cardiac veins as usual.

§ Abernethy (*loc. cit.*) and other cases by Fiorati, Sandifort, CaillIot, J. F. Meckel, Bernhard, Otto, &c., quoted in Quain's Arteries, p. 18.

‖ A specimen in the Museum of University College, which is described and represented in Prof. Quain's "Anatomy of the Arteries" (p. 17, plate 5. fig. 3). Haller in the right fœtus of a double monster (De Monstri Dissection, i. 1739; Opera Minora, t. iii. p. 102). For references to other cases, see a paper by Dr. Watson, Med. Gazette, June, 1836, p. 393. Also Mr. W. Clapp, Med. Gazette, Jan. 1850.

Transposition of the great anterior veins may be further complicated by subordinate varieties, as for example, in the intercostal systems; and it is interesting to find that one of the most remarkable of the deviations met with in the azygos vein when holding its customary position, has been observed also in the transposed vein; viz. its excessive enlargement to enable it to return the blood from the lower half of the body, in cases where the inferior cava is deficient, and is represented only by the trunk of the hepatic veins*.

Lastly, the great anterior veins do not appear ever to undergo transposition, unless the heart itself be reversed†.

Group B. *The second anterior venous trunk, an azygos venous trunk existing on the left side, or by transposition on the right.*—This condition, which is regular in the Sheep, Ox, Goat, Pig, &c., has not, as far as I know, been met with as a deviation in the human subject, even in the most complex forms of transposition or malformation; but it is here referred to as one that may possibly be yet detected‡.

In the cases hitherto recorded as examples of a left vena azygos in Man, the unusual vein, as already fully particularized (pp. 156, 157), has ended in some of the branches or in the trunk of the vena cava superior. A true left vena azygos, however, sometimes exists in the human subject, in connection with an additional superior cava, as will immediately be shown.

Group C. *The second anterior venous trunk, an additional vena cava superior.*

a. Without transposition. In these cases the heart and great vessels, as well as the other viscera, holding their usual position, the superadded vein is a *left superior cava*. This condition constitutes that interesting variety of the great anterior veins commonly named *double vena cava superior*, in which the arrangement of the vessels

* Herholdt (Abhandlung der K. Acad. zu Kopenhagen, 1818).

M^c^Whinnie (London Med. Gazette, 1840). The preparation is in St. Bartholomew's Hospital Museum, and is figured in Quain's "Anatomy of the Arteries," &c. (pl. 5. fig. 4). In both of these instances the transposed azygos receives all the branches of the inferior cava excepting the hepatic veins, and turns over the left bronchus to end in the ordinary upper cava, which, however, is on the left side.

† In an interesting case recorded by Wilson in the Philosophical Transactions, a vena cava superior, together with a perfect vena azygos, is found on the left side only of the thorax. This does not appear to have been an example of transposition of the right vein over to the left side; but rather one in which, the heart being reduced to a single auricle and a single ventricle and not transposed, the ordinary right upper cava is entirely wanting, whilst a true *left* upper cava alone exists, pursuing, as usual, a circuitous course to the heart (Philosophical Transactions, 1798, p. 346, with a plate). A case of ectopia cordis. The child lived seven days.

Standert (Philosophical Transactions for 1805, Part II. p. 228) gives an account of a child's heart, with undivided auricles and ventricles, in which the same condition of the veins, as far as can be understood from the figure, appears to have existed.

‡ Could the statement and figures of Vieussens (*loc. cit.*) be considered free from *all* doubt, the so-called *vein of the pericardium*, which returned the blood from the outside of that sac, and descended in the position of the oblique vein into the coronary sinus, might be conceived to have been a true left azygos venous trunk, formed by a persistent left canal of Cuvier (see p. 147).

resembles that observed in the Elephant, in many of the Rodentia, the Marsupials and some other Mammalia.

In these cases the ordinary right superior cava is smaller than usual, being assisted by the additional vein on the left side. This left upper cava, generally smaller than the right one, invariably descends over the aortic arch, and afterwards in front of the root of the left lung, beneath which it turns backwards and then runs along the base of the heart to reach the right auricle.

Nearly thirty examples of this condition are on record, and to that list I am enabled to add two more cases, which will be here described. For convenience of reference they may be tabulated in the following form.

Tabular View of Examples of Double Vena Cava Superior in the Human Subject.

Number in succeeding account.	Name of observer.	Date.	Sex and age.	Simple, or with other malformations.	Transverse branch present or not.	Azygos veins.	Figured or not.	Remarks.
0.	Bartholine	1641.						A doubtful case.
1.	St. Thomas's		Adult		A cross branch?	Right.		
2.	Boehmer and Theune	1763.	Male, 11 years		None	Right and left	Figured	
3.	Haller	1739–1762.	Fœtus	Double monster	None		Figured	
4.	Murray	1781.	Female, 60 years.		None	Right	Figured	
5.	Ring	1805.	Female, 1 year	Auricles not divided	?		Figured	
6.	Lemaire	1808.	Female, 30 years.	Auricles communicating	?			Rather doubtful case.
7.	Niemeyer	1814.	Fœtus	Much deformed	?		Figured	
8.	Meckel	1816.	Fœtus	Monstrous	?			
9.	Meckel	1816.	Fœtus	Monstrous	?			
10.	Meckel	1818.	Fœtus	Monstrous	?			
11.	Meckel	1820.	?		None (?)		Figured	
12.	Béclard	1816.	Adult		None (?)	Right and left (?)		
13.	Bock and Cerutti		Adult					Original description not referred to. Ditto.
14.	Hesselbach		Adult					Rather doubtful case.
15.	Weese	1819.	Fœtus	Ectopia cordis	?			
16.	Weese	1819.	Fœtus	Ectopia cordis	?			
17.	Weese	1819.	Fœtus	Ectopia cordis	None		Figured	
18, 19.	Wirtensohn	1825.	Fœtus, double	Monsters	None	Right	Figured	
20.	Wehrde	1826.	Fœtus	Monster				Original account not referred to.
21.	Breschet	1827.	Male adult		?			
22–24.	Breschet	1827.	Fœtuses	Ectopia cordis	?			
25.	Otto	1830.	Fœtus	Malformed	?			
26.	Otto	1830.	Fœtus	Malformed	?			
27.	Otto	1830.	?		?			
28.	Houston	1831.	Adult		?			
29.	Sharpey	1844.	Adult		A cross branch	Right and left	Figured	
30.	Author	1849.	Male, 56 years		A cross branch	Right and left	Figured	
31.	Author	1849.	Female, 5 years	Malformed	?			

Omitting Bartholine's case as doubtful, the thirty one remaining examples may be thus distributed. Sixteen have occurred in fœtuses more or less malformed; the age and condition of the subjects of two are uncertain; and, in two others, though the individual had lived in one case for a year, and in the other for five years, there was some accompanying defect in the heart; so that, including Lemaire's case, not more than *eleven* examples of additional superior cava have yet been observed in the *adult*, uncomplicated by other deviations from the ordinary condition of the heart.

(St. Thomas's, Bœhmer and Theune, Murray, Lemaire (?), Meckel, Béclard, Breschet, Otto, Houston, Sharpey, the Author*.)

Only those examples of left vena cava superior can be included in the present group, in which the cross branch at the root of the neck has been duly formed, the instances in which that characteristic preliminary step in the development has not taken place, being referable to the *second* class of peculiarities of the great anterior veins. Unfortunately, the descriptions of most of the known examples of double vena cava superior are incomplete, particularly as regards the existence of the transverse branch in the neck, and the condition of the azygos veins.

In two instances only is the presence of the cross branch placed beyond a doubt (Nos. 29, 30)†.

In six cases, in which the vessels appear to have been examined and preserved sufficiently high up in the neck to have determined the point one way or the other, the cross branch seems as certainly to have been wanting (Nos. 2, 3, 4, 17, 18, 19)‡.

With regard to a *large number* of the examples, it is quite impossible, on reference to the descriptions or figures, to decide whether any transverse branch had ever existed or not (Nos. 1, 5, 7, 8, 9, 10, 11, 12, 16, 21, 22, 23, 24, 25, 26, 27, 28, 31)§.

* Rosenthal's case, already mentioned (p. 154), has usually been considered an example of additional left superior cava, but it appears rather to be one of prolonged subdivision of the right vena cava. Le Cat's interesting specimen (p. 158) might be considered to have been an example of a small left upper cava, closed at its lower end.

† No. 29. Professor Sharpey met with this specimen in Edinburgh in 1833 or 1834. The preparation (injected and dried) is now in the Museum of Anatomy of University College, London. It is represented in Prof. R. Quain's work on the Arteries, &c. (pl. 58, figs. 9, 10, pp. 371, 432). In all respects in which it can be compared, it resembles the following case, No. 30.

No. 30. The Author's example, described in pages 162–164.

‡ The references to these six cases are given in pages 164, 165.

§ No. 1. In the Museum of St. Thomas's Hospital there exists a specimen of double vena cava superior. The preparation in question, No. 1178, is an adult heart, which has been injected and dried. The cavities, which are now empty, are laid open. The left vena cava superior is smaller than the right, excepting its intrapericardial portion, which is much dilated. There are indications of a transverse branch, but its existence cannot now be confidently asserted. The azygos vein, which is of ordinary size, opens as high as usual in the right superior cava. The middle cardiac vein opens directly into the auricle. The coronary vein appears to be small. There is no azygos visible on the left side. The wide orifice of the left cava has, on its upper and right border, a narrow ridge, but there is no Thebesian valve. A small perforated Eustachian valve exists. Cheselden (Philosophical Transactions, 1713, vol. xxviii. p. 282) has described "a heart with the vena azygos inserted into the right auricle, and the descending cava coming round the basis of the heart, above the aorta and pulmonary vessels, to enter the auricle at the lower part with the ascending cava." This case has usually been regarded as an example of double vena cava superior. The preparation at St. Thomas's, the history of which is not known, but which Mr. South informs me is one of the oldest in the collection, may possibly be the specimen described by Cheselden; but as his account is so brief, and no drawing accompanies it, the point must remain doubtful. There is a discrepancy between the specimen and the account in the Philosophical Transactions in regard to the termination of the vena azygos.

No. 5. Ring (Med. and Phys. Journal. London, vol. xiii. 1805, p. 120, with two figures). The preparation is in St. Thomas's Hospital Museum. This case shows a right and a left superior cava, with want of sepa-

In three instances, no access has been had to the original descriptions (Nos. 13, 14, 20)*.

The three remaining cases, though usually regarded as instances of superadded left superior cava, are somewhat doubtful examples of this variety (Nos. 0, 6, 15)†.

Further, the condition of the azygos veins is accurately known in only four cases (Nos. 2, 4, 29, 30).

In every instance, the course and connections of the left vena cava superior, so far as can be ascertained from the descriptions, correspond entirely. Reserving for the present the six cases in which the absence of the cross branch seems to be certain, I may here describe, as a characteristic example of double vena cava superior, accompanied with the cross branch, the specimen met with by myself.

The subject of this case (No. 30), a male aged fifty-six years, had not suffered from any disease of the heart. That organ is rather large: the right vena cava superior (Plate VI. *h*) is smaller than usual, and pursues its accustomed course to the

ration of the auricles. Had the interauricular septum been formed, the left vein, which is now described as opening into the *left* auricle, would probably have had its orifice directed into the right auricle. Similar instances are recorded by Weese and Breschet, Nos. 16 and 23, 24.

No. 7. Niemeyer (De fœtu puellari edito abnormitatis exemplo. Halæ, 1814, cum fig.). The left cava superior is said to have descended to join the inferior cava, reminding one of Cheselden's description.

No. 8 to 11. Meckel (Tabul. Anat. Path. 1820, tab. x. figs. 6, 7); two other cases (Hand. der Anat. Path. 1816, vol. ii. p. 125); and one (Archiv. f. d. Physiolog. vol. iv. p. 479, 480).

No. 12. Béclard (Bull. de la Soc. de Med. 1816, vol. v. p. 115).

No. 16. Weese (De Ectopia cordis, 1818, sect. 19). The same case is in Walter's Museum Anat. P. i. p. 135, No. 826; and had been partially described by Buettner.

No. 21 to 24. Breschet (Le Système Veineux, 1827, p. 2, note 1). One example was in an adult male. Was this Béclard's specimen? The other examples are in malformed fœtuses (Mém. sur l'Ectopie, &c.; and Répertoire d'Anat. et Phys., &c. t. ii. p. 12 and p. 17).

No. 25 to 27. Otto (Beobachtung. ii. p. 69, and Verzeichniss, No. 2874). (Lehrbuch, &c., p. 344.) One example in an otherwise perfect subject. The two others in fœtuses malformed.

No. 28. Houston's Catalogue of the Museum of the College of Surgeons, Dublin (vol. i. p. 58, B. b. 92).

No. 31. The Author. This heart, which is described at page 164, was presented to me by Dr. R. Dawson Harling.

* These cases are referred to in Otto's Lehrbuch der Pathol. Anat. 1830, vol. i. p. 347, note 13, as follows:—

No. 13. Bock in Cerutti's Pathol. Anat. Museum, B. i. H. 3. p. 50.

14. Hesselbach, Beschreibung der Pathol. Präparate zu Würtsburg, p. 229.

20. Wehrde, Diss. Anat. Path. de Monstro rariore humano. Halæ, 1826, p. 11.

† No. 0. Bartholine, Th. (Histor. Anatom. Montpelier, 1641, Hist. 84. Cent. ii. p. 322). This is quoted as an undoubted example by Otto (*op. cit.* p. 347, note 13), but the statement of Bartholine is not clear. He says, "that illustrious anatomist A. Falconbridge once showed me in a human dissection, an additional vein near the vena cava, similar to it, and which he considered a second cava."

No. 6. Lemaire (Bull. des Scien. Med. vol. v. 1808, p. 21). This (as already stated, p. 158) is described by Lemaire as an instance of the coronary vein ending in an *unusual left pulmonary vein*; but on careful perusal of the description, it appears more probable that the vein supposed to be pulmonary was really a *left vena cava superior*. There was a greater chance of error in this case, owing to there having been extensive adhesions of the pericardium.

No. 15. Weese (*op. cit.* sect. 45).

right auricle. The transverse branch in the neck (*d*) is not half the size of either jugular vein. It crosses over the commencement of the great arteries of the head and neck, and opens into the lateral venous trunks, somewhat below the point of junction of the jugular and subclavian veins of each side. This circumstance (observed also in Professor SHARPEY's preparation) is interesting when considered in relation to the position of the cross branch in the embryo, and to the mode of formation of the right innominate vein.

From opposite the left end of this cross branch, the additional superior cava (*fvlos*) descends upon the aorta, to the front of the root of the left lung, and crossing the corresponding vessels, reaches the side of the left auricle immediately behind the appendix; then turning backwards under the lowermost pulmonary vein in close contact with the auricle, it runs obliquely inwards beneath the base of the heart along the auriculo-ventricular furrow; and finally opens by a wide orifice into the right auricle, to the left of, and somewhat before the inferior cava, *i. e.* in the ordinary situation of the orifice of the coronary sinus.

The azygos vein exists on the right side, and on the left there is a small vein opening into the left cava, about 1½ inch below the cross branch, and close above the root of the lung: this small vein is a left azygos formed by the persistence of a part of the left cardinal vein: it fulfils the office of the left superior intercostal vein. The azygos and this small left azygos are also seen in Professor SHARPEY's preparation.

From the cross branch down to the root of the lung, *i. e.* outside the pericardium, the left cava is rather narrower than the right. It is placed close beneath the pleura, and supports upon its outer side the left phrenic nerve (14). It rests first upon the left carotid and subclavian arteries, and then on the arch of the aorta. The par vagum (13) descends further back than the vein, and gives off a branch, which accompanies the vessel to the heart. On a level with the upper border of the pulmonary artery, the vein pierces the fibrous layer of the pericardium (11, 11).

Within the pericardium, as may be noticed in all the cases which have been fully described, the left vena cava becomes very much dilated. As it passes from the left pulmonary artery to the root of the subjacent pulmonary vein, it is lodged (*v*) in a tube-like fold of the serous membrane, the analogue of the *vestigial fold*. On the side and back of the left auricle (*lo*), and afterwards along the course of the auriculo-ventricular groove (*s*), the vessel is everywhere covered and bound down by the serous layer of the pericardium, and has muscular walls.

In turning horizontally to the right it receives the coronary vein (*g*), which appears small, and courses rather over the left border of the ventricle than comes from between the ventricle and the auricle. Further on, a posterior (*p*) and then the middle (*m*) cardiac vein enter it from below. The large vessel itself (*o*) occupies the place of the short oblique vein usually found on the back of the left auricle. The lower dilated part of the left vena cava superior (*s*), occupying the place of the coronary sinus, is distinctly muscular, its fibres for the most part being circular and ap-

parently blending with those of both auricles. There are no valves along its course, but the mouth of each of its cardiac branches is guarded with a fine valve, that of the coronary vein being the largest. The wide orifice of the vessel into the right auricle is marked above, below and to the right, by a slight rim, but there is no Thebesian valve, the absence of which, in this and all the other examples of double vena cava superior in which the point is capable of being determined (Nos. 1, 4, 12, 30, 31), suggests a comparison with the fact that it is also absent in those large quadrupeds which have a left vena cava superior or a left azygos venous trunk. The Eustachian valve is small and perforate; its left cornu does not reach the lower border of the fossa ovalis, owing, as it were, to the intervention of the large orifice of the left superior cava. The foramen ovale is quite closed.

The second example (No. 31) of double vena cava superior which I have to mention, occurred in the heart of a child between four and five years of age; in the ventricular portion of which there are some defects. The auricles, however, are perfectly shut off from each other. The lower part only of the left superior cava is present in the preparation, that vessel having been divided opposite the left pulmonary veins: it is very large and muscular, and receives the coronary and one other principal cardiac vein, the orifices of both being provided with valves. The opening of the vessel into the auricle is marked by a sharp border; but, as in other cases, the Thebesian valve is wanting. So, too, is the Eustachian valve.

b. *With transposition.*—There is, so far as I am aware, but one instance on record of the occurrence of double vena cava superior, together with transposition of the viscera. In this case the superadded vein is of course on the right side: a small vena azygos exists on that side, and ends in the right vena cava*.

CLASS II. TRANSVERSE BRANCH WANTING.

A failure in the preliminary step of the development of a cross branch in the neck necessarily implies the non-occlusion of either of the lateral primitive veins; for, though two superior cavæ may coexist with the transverse communication in the neck, yet, when the latter is absent, each primitive vein must continue to return the blood from its own side of the upper half of the body.

In such instances the characteristic cross branch of the mammalian venous system is wanting; the condition of the great anterior veins is like that of birds; and there is *no metamorphosis* excepting what is due to changes of size and position in the four simple lateral primitive veins typical of the vertebrate animal. Transposition has not been noticed in connection with this variety.

The best illustration of deficiency of the cross branch occurs in a case (No. 2)†

* Sir A. Cooper, in Dr. Watson's paper, Medical Gazette, June 1836, p. 394. The specimen is now in the Museum of the Royal College of Surgeons.

† No. 2. Boehmer (Observ. Anat. rarior. fasciculi. Præfat. p. xii.). Theune (De confluxu trium cavar. in cord. atrio dextro, &c. Halæ, 1763, with a figure. Republished, Amsteld. 1764).

briefly recorded by Bœhmer, and subsequently clearly described and figured by Theune. The subject was a boy, aged 11 years. The vessels of the thorax and neck were injected with wax; and, though numerous small thyroid branches descended to the jugular veins, there was no appearance whatever of a transverse branch across the neck. Besides this, the case is interesting as affording a distinct example of the presence of both azygos veins ending, one in each of the superior cavæ. The right azygos was rather higher than usual; the *left* azygos, a little lower down than the right one, could be followed along the left side of the vertebræ as low as the lumbar veins in the abdomen.

Another specimen of double superior cava in an adult (No. 4)*, in which the cross branch must be regarded as wanting, has been elaborately described and represented in two figures by Adolphe Murray. With the exception of this deficiency of the cross branch, and of apparent absence of the left azygos also, the case resembles No. 30. The coronary vein is described as wanting: but it was represented by a branch which, as in case No. 30, turned over the left border of the heart.

The four remaining examples were in malformed fœtuses, carefully dissected by Haller, by Weese and by Wirtensohn (Nos. 3, 17, 18 and 19)†.

Finally, such extreme cases of malformation as those in which (as in acephalous or almost shapeless fœtuses) the primitive plan of the venous system is altogether abrogated, do not here come under consideration.

Description of the Plates.

PLATE I.

Fig. 1. Sketch of the human heart, seen on its left and posterior aspect, together with the great blood-vessels and a piece of the left lung:—reduced one-fifth. The coronary sinus, the great coronary vein, and the other posterior cardiac veins have been slit up. 1. The right auricle. 2. The left auricle. 3. The ventricular portion of the heart. 4. Portion of the root of the left lung. 8. The aorta. 9. The pulmonary artery. 10, 10. The left pulmonary veins. 11, 11. The cut edge of the pericardium. *c*. Vena cava superior. *e*. Vena cava inferior. *g*. Great coronary vein. *m*. Middle cardiac vein. *p, p*. Posterior cardiac veins. *s*. Coronary sinus laid open,

* Murray, Ad. (Neue Schwedische Abhandl. aus der Naturlehre, &c., band 2, p. 283, with two plates). He refers to Bartholine, Cheselden and Haller; and also to Bœhmer and Theune, whose observation he considers the only one like his own.

† No. 3. Haller (Descript. Monstr. dissect. i. 1739. Oper. Minora, t. iii. p. 102. 5. Tabul. xv.). The peculiarity in question occurs in the left fœtus only of a double monster. No. 17. Weese (*op. cit.* sect. 47, p. 30. Tabul. vi. fig. 1). This was a case of Ectopia cordis which had been previously examined by Kuestner. The left veins *did not join* those of the right side, but descended separately to the heart by a left venous trunk. Nos. 18, 19. Wirtensohn, Diss. duor. Monstr. dupl. humanor. Berol. 1825, p. 23.

to show the large valve *x*, at the mouth of the great coronary vein (*g*), and smaller valves at the mouths of the posterior (*p*, *p*) and middle (*m*) cardiac veins. *t*. Orifice of the coronary sinus into the right auricle, with the Thebesian valve. *o*, *l*, *v*. Remains of the left primitive venous trunk above the coronary sinus, consisting of *o*, a small oblique auricular vein; *l*, lines or streaks on the wall of the left auricle; and *v*, a small duplicature of the serous layer of the pericardium, passing between the left pulmonary artery and the subjacent pulmonary vein, which is referred to in subsequent plates as the *vestigial fold of the pericardium*.

Fig. 2. Sketch of the back of the Sheep's heart; the great vessels being cut off short. 1, 2, 3, 8, 10, 10, *c* and *e* refer to the same parts as in fig. 1. *s*, *s'*. The trunk of the left azygos vein laid open, showing the large valve (*x*) at the entrance of the great coronary vein (*g*), and the smaller valves at the mouths of the veins marked *p*, *m*, *p*. The portion of the left azygos vein marked *s'*, is analogous to the coronary sinus in Man, *s*, fig. 1. *t*. Orifice of the left vena azygos, destitute of a Thebesian valve.

PLATE II.

Development of the great anterior veins in the embryo of the Sheep. Each figure is magnified two diameters. Corresponding letters of reference are used in common; viz. *a*. The right, and *a'*, the left primitive jugular vein; *o*, the occluded portion of the left primitive jugular vein. *b*. The right, and *b'*, the left cardinal vein. *c*. The right, and *c'*, the left canal of Cuvier. *d*. The transverse branch across the root of the neck, afterwards the left innominate vein. *e*. The trunk of the future vena cava inferior. 1. The right auricle. 2. The left auricle. 3. The ventricles. 4, 4'. The lungs, right or left. 5, 5'. The Wolffian bodies, right or left. 7. The stomach.

Figs. 1, 2, 3. Lateral and front views of an embryo, $\frac{1}{10}$ths of an inch long. The great anterior veins are symmetrical, and consist of four lateral trunks, viz. two jugular and two cardinal veins, ending in the two Cuvierian canals. The jugular veins are short and vertical; the cross branch is wanting, but two little points are seen projecting from the inner side of the jugular veins where this transverse vessel is to appear. The dotted lines in figs. 1 and 3 indicate the outline of the liver, which has been removed.

Fig. 4. Embryo, $\frac{7}{10}$ths of an inch long. The jugular veins elongated, and beginning to approach each other opposite the place of the future transverse branch, which could not be traced quite across the neck. The cardinal veins are smaller, owing to the wasting of the Wolffian bodies.

Fig. 5. Heart of an embryo, 1 inch long. The cross branch distinct, consisting of a fine vessel, which is wider at each end than in the middle.

Fig. 6. Embryo, $\frac{8}{10}$ths of an inch, and fig. 7, embryo, $1\frac{3}{10}$ths of an inch long. The jugular veins have become more closely approximated at the root of the neck. The

cross branch is shorter and wider. The lower part of each primitive jugular, below the cross branch, inclines downwards and outwards, lying upon the pericardium. The left cardinal vein is still further reduced in size, but no occlusion has yet taken place.

Fig. 8. Embryo, 1 inch and $\frac{3}{10}$ths long. In this embryo, and in embryo fig. 10, most part of the left lung has been cut away. The lower part of the left primitive jugular, extending from below the cross branch to the junction of the left cardinal vein and left canal of Cuvier, is occluded, and a fine opake cord (*o*) exists in its place. The left cardinal vein and left Cuvierian canal now form the left vena azygos, as in the adult, the intrapericardial portion of which is seen to cross the left pulmonary vessels, and is lodged in a fold of the serous membrane. The cross branch now passes obliquely over to the right side, and forms the left innominate vein, which ends in the lower part of the right jugular, now the vena cava superior.

Fig. 9. Back of the heart of an embryo, $1\frac{1}{4}$ inch long, to show the differences, in size, length and direction, between the right and left Cuvierian canals, after the partial occlusion of the left jugular. The different heights of the right and left azygos veins are also exhibited.

Fig. 10. Embryo, $1\frac{1}{2}$ inch in length; it shows the state of the primitive anterior venous trunks after the completion of their metamorphosis, and therefore resembles the adult condition.

PLATE III.

Development of the great anterior veins in the human embryo. Each figure is magnified two diameters. Corresponding letters of reference are used in all cases, viz. *a*. The right, and *a'*, the left primitive jugular vein. *b*. The right, and *b'*, the left cardinal vein. *c*. The right, and *c'*, the left canal of Cuvier, or its pervious remnants. *c''*. Occluded portion of the left canal of Cuvier. *d*. The transverse branch in the neck, afterwards the left innominate vein. *e*. The vena cava inferior. *h*. The vena cava superior. *i*. Trunk of the left superior intercostal vein. 2. Left auricle. 3. Ventricular portion of the heart. 4. Lung, or part of lung. 5. Wolffian body. 6. Part of the liver. 7. The stomach.

Figs. 1, 2. Left and right lateral view of an embryo, $\frac{1}{3}\frac{7}{2}$ths of an inch in length. The cross branch is fully formed and very wide. The cardinal veins have diminished with the wasting of the Wolffian bodies; but no occlusion having taken place, the great lateral venous trunks are still symmetrical. N.B. Embryo damaged before dissection.

Fig. 3. Embryo, $1\frac{3}{10}$ths of an inch long. The lower part of the left primitive jugular (below the cross branch) is elongated, and, as well as the left Cuvierian canal, is beginning to shrink.

Fig. 4. Embryo, $1\frac{1}{10}$ths of an inch long. The left primitive jugular vein below the

cross branch is entirely occluded, and also the succeeding part of the left Cuvierian canal, the lower end of which, however, remains pervious as a little conical pouch (c') on the back of the left auricle. A fine cord (c'') occupies the place of the occluded vessel. The left cardinal vein has disappeared. The cross branch, now oblique in direction, forms the left innominate vein (d), which ends in the vena cava superior (h).

Fig. 5. Embryo, $1\frac{5}{10}$ths of an inch long from vertex to coccyx, and fig. 6, embryo, 3 inches from vertex to coccyx. In these embryos, a portion of the left primitive jugular vein immediately below the cross branch remains open, though reduced in size, and forms the trunk of the left superior intercostal vein (i); the succeeding portion is occluded and forms a fine semitransparent cord, which is continuous through the pericardium, with the occluded part of the left canal of Cuvier (c''). This latter lies in a fold of the serous membrane in front of the left pulmonary vessels, and descends on the back of the left auricle to the conical pouch (c') above mentioned. The left cardinal vein (b') in fig. 6, relatively very much diminished in size, appears to form a branch of the left superior intercostal vein.

PLATE IV.

Several views of the hearts of human embryos to show the gradual alterations in the size, length and direction of the two canals of Cuvier, and the particular metamorphosis of the left canal. Figs. 1 to 6 and figs. 8, 10 and 11 are views of the under surface of the organ. Figs. 7 and 9 are representations of its left side. All the figures, excepting fig. 11, are shown magnified two diameters.

The letters of reference employed in the several figures are as follows. *a*. Right and a' left jugular. *c*. Right, and c', left canal of Cuvier. c''. Occluded portion of this canal. *d*. Cross branch in the neck, or left innominate vein. *e*. Vena cava inferior. *f v l o s*. Parts occupying the place of the left canal of Cuvier, viz. *f*. Fibrous bands beneath the left pleura outside the pericardium, *v*. Vestigial fold of the pericardium, *l*. Lines or streaks on the back of the left auricles, *o*. Oblique auricular vein, and *s*. Coronary sinus. *g*. Great cardiac or coronary vein. *h*. Vena cava superior. 1. Right, and 2, left auricle. 3. Ventricles. 4. Part of left lung. 8. Aorta. 9. Pulmonary artery. 10. Left pulmonary veins. 11. Cut edge of the pericardium.

Figs. 1, 2. Heart of an embryo, $\frac{1}{10}$ths of an inch long. Figs. 3, 4. Heart of an embryo, 1 inch long. Figs. 5, 6. Heart of an embryo, $1\frac{6}{10}$ths of an inch long. In these figures, viz. 1, 3 and 5, the right canal of Cuvier (c), is seen progressively to become shorter, wider and more vertical: the left canal (c'), which is shown opened in figs. 2, 4 and 6, becomes longer, narrower, and more circuitous in its course to the right auricle.

Fig. 7, left side, and fig. 8, the under surface of the heart of an embryo, $2\frac{1}{2}$ inches long. The cavities of the heart are filled with hardened blood. The upper occluded part of the left canal of Cuvier (c'') is well seen; and also the transformation of its

lower portion into a small oblique vein and the coronary sinus (*s*), into which, at its junction with the oblique vein, the coronary vein (*g*) enters.

Fig. 9. Outline plan carefully constructed from the heart of an embryo, measuring 5 inches from the vertex to the coccyx. The essential stages of the metamorphosis of the left primitive venous trunks are so complete, that the parts now representing it are nearly the same as in the adult condition, viz. the trunk of the left superior intercostal vein (*i*), the vertical fibres beneath the left pleura (*f*), the vestigial fold (*v*), and the lines or streaks (*l*) on the left auricle. The lower persistent portion of the left canal of Cuvier is transformed into a short oblique vein (*o*) and the coronary sinus (*s*), which are only partly seen, and which are joined by the great cardiac or coronary vein (*g*).

Fig. 10. Heart of the same embryo. The lines or streaks (c''), the oblique vein, the coronary sinus (*s*) and the coronary vein (*g*) appear almost as in the adult heart.

Fig. 11. Heart of a small fœtus, still-born at the full period. The drawing is of the natural dimensions. The metamorphosed parts are easily recognized. The coronary vein (*g*) and sinus (*s*) are slit up, to show the commencing valve at their point of junction, and the place of opening of the oblique vein (*o*), which is continued up into the line or streak (*l*).

PLATE V.

Sketch of the under surface and left side of the heart, great blood-vessels, and root of the left lung, from a female aged 19; exhibiting the remains of the left anterior primitive vein, as ordinarily seen in the adult human heart. 1, 2, 3, 4, 8, 9, 10, 10, 11 and *e*, refer to the same parts as in Plate I. fig. 1. 13. The left vagus nerve. *d*. Left innominate vein, formed by the primitive cross branch and part of left primitive jugular. *i*. Trunk of the left superior intercostal vein, formed by the part of the metamorphosed left jugular vein situated immediately below the cross branch in the neck. *f*. Indistinct fibrous bands, mixed with small vessels and nervous cords, shown after removal of the pleura, lying in the track of the previously existing vein, and passing down to the root of the left lung, and thence through the pericardium into the fold marked *v*. *v*. The *vestigial fold* of the pericardium, persisting after the occlusion of the corresponding part of the left canal of Cuvier. *l*. Lines or streaks on the wall of the left auricle, descending from the vestigial fold to a small oblique vein, marked *o*. This oblique vein (*o*) enters the coronary sinus (*s*) close by the valved orifice of the coronary vein (*g*): together with the sinus, it forms the lower persistent pervious portion of the left primitive vein or canal of Cuvier.

PLATE VI.

Sketch of the under surface and left side of the heart and great vessels of a man, aged 56 years, in which there is a second superior cava on the left side, constituting

what is termed a case of "double vena cava superior." 1, 2, 3, 4, 8, 9, 10, 11 and *e*, refer to the same parts as in Plate I. fig. 1. 13. The vagus nerve. 14. Portion of the left phrenic nerve resting on the left vena cava superior. *d*. The cross branch at the root of the neck passing across below the place of junction of the subclavian and jugular veins. *h*. Part of the right vena cava superior. *i*. A left superior intercostal vein crossing over the descending aorta and acting as a small left azygos vein. *f*, *v*, *l*, *o* and *s*, are placed on the successive portions of the left vena cava, or persistent left primitive vein, which correspond with the successive remains met with in the ordinary condition, viz. *f*, with the subpleural fibrous bands; *v*, with the vestigial fold between the left pulmonary artery and veins; *l*, with the lines on the back of the left auricle; *o*, with the oblique vein; and *s*, with the coronary sinus. Into this latter there open, *g*, the great coronary vein, *p*, a posterior, and *m*, the middle cardiac vein.

VII. *Experimental Researches in Electricity.—Twenty-third Series.* By MICHAEL FARADAY, *Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. Pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, &c. &c.*

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§ 29. *On the polar or other condition of diamagnetic bodies.*

2640. FOUR years ago I suggested that all the phenomena presented by diamagnetic bodies, when subjected to the forces in the magnetic field, might be accounted for by assuming that they then possessed a polarity the same in kind as, but the reverse in direction of, that acquired by iron, nickel and ordinary magnetic bodies under the same circumstances (2429. 2430.). This view was received so favourably by PLÜCKER, REICH and others, and above all by W. WEBER*, that I had great hopes it would be confirmed; and though certain experiments of my own (2497.) did not increase that hope, still my desire and expectation were in that direction.

2641. Whether bismuth, copper, phosphorus, &c., when in the magnetic field, are polar or not, is however an exceedingly important question; and very essential and great differences, in the mode of action of these bodies under the one view or the other, must be conceived to exist. I found that in every endeavour to proceed by induction of experiment from that which is known in this department of science to the unknown, so much uncertainty, hesitation and discomfort arose from the unsettled state of my mind on this point, that I determined, if possible, to arrive at some experimental proof either one way or the other. This was the more needful, because of the conclusion in the affirmative to which WEBER had come in his very philosophical paper; and so important do I think it for the progress of science, that, in those imperfectly developed regions of knowledge, which form its boundaries, our conclusions and deductions should not go far beyond, or at all events not aside from the results of experiment (except as suppositions), that I do not hesitate to lay my present labours, though they arrive at a negative result, before the Royal Society.

2642. It appeared to me that many of the results which had been supposed to indicate a polar condition, were only consequences of the law that diamagnetic bodies tend to go from stronger to weaker places of action (2418.); others again appeared to have their origin in induced currents (26. 2338.); and further consideration seemed

* POGGENDORFF's Annalen, January 7, 1848, or TAYLOR's Scientific Memoirs, v. p. 477.

to indicate that the differences between these modes of action and that of a real polarity, whether magnetic or diamagnetic, might serve as a foundation on which to base a mode of investigation, and also to construct an apparatus that might give useful conclusions and results in respect of this inquiry. For, if the polarity exists it must be in the particles and for the time permanent, and therefore distinguishable from the momentary polarity of the mass due to induced temporary currents; and it must also be distinguishable from ordinary magnetic polarity by its contrary direction.

2643. A straight wooden lever, 2 feet in length, was fixed by an axis at one end, and by means of a crank and wheel made to vibrate in a horizontal plane, so that its free extremity passed to and fro through about 2 inches. Cylinders or cores of metal or other substances, 5½ inches long and three-quarters of an inch diameter, were fixed in succession to the end of a brass rod 2 feet long, which itself was attached at the other end to the moving extremity of the lever, so that the cylinders could be moved to and fro in the direction of their length through the space of 2 inches. A large cylinder electro-magnet was also prepared (2191.), the iron core of which was 21 inches long and 1·7 inch in diameter; but one end of this core was made smaller for the length of 1 inch, being in that part only 1 inch in diameter.

2644. On to this reduced part was fixed a hollow helix consisting of 516 feet of fine covered copper wire: it was 3 inches long, 2 inches external diameter, and 1 inch internal diameter: when in its place, 1 inch of the central space was occupied by the reduced end of the electro-magnet core which carried it; and the magnet and helix were both placed concentric with the metal cylinder above mentioned, and at such a distance that the latter, in its motion, would move within the helix in the direction of its axis, approaching to and receding from the electro-magnet in rapid or slow succession. The least and greatest distances of the moving cylinder from the magnet during the journey were one-eighth of an inch and 2·2 inches. The object of course was to observe any influence upon the experimental helix of fine wire which the metal cylinders might exert, either whilst moving to or from the magnet, or at different distances from it*.

2645. The extremities of the experimental helix wire were connected with a very delicate galvanometer, placed 18 or 20 feet from the machine, so as to be unaffected directly by the electro-magnet; but a commutator was interposed between them. This commutator was moved by the wooden lever (2643.), and as the electric currents which would arrive at it from the experimental helix, in a complete cycle of motion or to and fro action of the metal cylinder (2643.), would consist of two contrary portions, so the office of this commutator was, sometimes to take up these portions in succession and send them on in one consistent current to the galvanometer, and at

* It is very probable that if the metals were made into cylinders shorter, but of larger diameter than those described above, and used with a corresponding wider helix, better results than those I have obtained would be acquired.

other times to oppose them and to neutralize their result; and therefore it was made adjustible, so as to change at any period of the time or part of the motion.

2646. With such an arrangement as this, it is known that, however powerful the magnet, and however delicate the other parts of the apparatus, no effect will be produced at the galvanometer as long as the magnet does not change in force, or in its action upon neighbouring bodies, or in its distance from, or relation to, the experimental helix; but the introduction of a piece of iron into the helix, or anything else that can influence or be influenced by the magnet, can, or ought to, show a corresponding influence upon the helix and galvanometer. My apparatus I should imagine, indeed, to be almost the same in principle and practice as that of M. WEBER (2640.), except that it gives me contrary results.

2647. But to obtain correct conclusions, it is most essential that extreme precaution should be taken in relation to many points which at first may seem unimportant. All parts of the apparatus should have perfect steadiness, and be fixed almost with the care due to an astronomical instrument; for any motion of any portion of it is, from the construction, sure to synchronize with the motion of the commutator; and portions of effect, inconceivably small, are then gathered up and made manifest as a whole at the galvanometer; and thus, without care, errors might be taken for real and correct results. Therefore, in my arrangements, the machine (2643, &c.), the magnet and helix, and the galvanometer stood upon separate tables, and these again upon a stone floor laid upon the earth; and the table carrying the machine was carefully strutted to neighbouring stone-work.

2648. Again, the apparatus should itself be perfectly firm and without shake in its motion, and yet easy and free. No iron should be employed in any of the moving parts. I have springs to receive and convert a portion of the momentum of the whole at the end of the to and fro journey; but it is essential that these should be of hammered brass or copper.

2649. It is absolutely necessary that the cylinder or core in its motion should not in the least degree disturb or shake the experimental helix and the magnet. Such a shake may easily take place and yet (without much experience) not be perceived. It is important to have the cores of such bodies as bismuth, phosphorus, copper, &c., as large as may be, but I have not found it safe to have less than one-eighth of an inch of space between them and the interior of the experimental helix. In order to float, as it were, the core in the air, it is convenient to suspend it in the bight or turn of a fine copper wire passing once round it, the ends of which rise up, and are made fast to two fixed points at equal heights but wide apart, so that the wire has a V form. This suspension keeps the core parallel to itself in every part of its motion.

2650. The magnet, when excited, is urged by an electric current from five pairs of GROVE'S plates, and is then very powerful. When the battery is not connected with it, it still remains a magnet of feeble power, and when thus employed may be referred to as in the *residual state*. If employed in the residual state, its power may for

the time be considered constant, and the experimental helix may at any moment be connected with the galvanometer without any current appearing there. But if the magnet be employed in the excited state, certain important precautions are necessary; for upon connecting the magnet with the battery and then connecting the experimental helix with the galvanometer, a current will appear at the latter, which will, in certain cases, continue for a minute or more, and which has the appearance of being derived at once from that of the battery. It is not so produced, however, but is due to the *time* occupied by the iron core in attaining its maximum magnetic condition (2170. 2332.), during the whole of which it continues to act upon the experimental helix, producing a current in it. This time varies with several circumstances, and in the same electro-magnet varies especially with the period during which the magnet has been out of use. When first employed, after two or three days' rest, it will amount to eighty or ninety seconds, or more. On breaking battery contact and immediately renewing it, the effect will be repeated, but occupy only twenty or thirty seconds. On a third intermission and renewal of the current, it will appear for a still shorter period; and when the magnet has been used at short intervals for some time, it seems capable of receiving its maximum power almost at once. In every experiment it is necessary to wait until the effect is shown by the galvanometer to be over; otherwise the last remains of such an effect might be mistaken for a result of polarity, or some peculiar action of the bismuth or other body under investigation.

2651. The galvanometer employed was made by RUHMKORFF and was very sensible. The needles were strengthened in their action and rendered so nearly equal, that a single vibration to the right or to the left occupied from sixteen to twenty seconds. When experimenting with such bodies as bismuth or phosphorus, the place of the needle was observed through a lens. The perfect communication in all parts of the circuit was continually ascertained by a feeble thermo-electric pair, warmed by the fingers. This was done also for every position of the commutator, where the film of oxide formed on any part by two or three days' rest was quite sufficient to intercept a feeble current.

2652. In order to bring the phenomena afforded by magnetic and diamagnetic bodies into direct relation, I have not so much noted the currents produced in the experimental helix, as the effects obtained at the galvanometer. It is to be understood, that the standard of deviation, as to direction, has always been that produced by an iron wire moving in the same direction at the experimental helix, and with the same condition of the commutator and connecting wires, as the piece of bismuth or other body whose effects were to be observed and compared.

2653. A thin glass tube, of the given size (2643.), $5\frac{1}{2}$ by $\frac{3}{4}$ inches, was filled with a saturated solution of protosulphate of iron, and employed as the experimental core: the velocity given to the machine at this and all average times of experiment was

such as to cause five or six approaches and withdrawals of the core in one second; yet the solution produced no sensible indication at the galvanometer. A piece of magnetic glass tube (2354.), and a core of foolscap paper, magnetic between the poles of the electro-magnet, were equally inefficient. A tube filled with small crystals of protosulphate of iron caused the needle to move about 2°, and cores formed out of single large crystals, or symmetric groups of crystals of sulphate of iron, produced the same effect. Red oxide of iron (colcothar) produced the least possible effect. Iron scales and metallic iron (the latter as a thin wire) produced large effects.

2654. Whenever the needle moved, it was consistent in its direction with the effect of a magnetic body; but in many cases, with known magnetic bodies, the motion was little or none. This proves that such an arrangement is by no means so good a test of magnetic polarity as the use of a simple or an astatic needle. This deficiency of power in that respect does not interfere with its ability to search into the nature of the phenomena that appear in the experiments of WEBER, REICH and others.

2655. Other metals than iron were now employed and with perfect success. If they were magnetic, as nickel and cobalt, the deflection was in the same direction as for iron. When the metals were diamagnetic, the deflection was in the contrary direction; and for some of the metals, as copper, silver and gold, it amounted to 60° or 70°, which was permanently sustained as long as the machine continued to work. But the deflection was not the greatest for the most diamagnetic substances, as bismuth or antimony, or phosphorus; on the contrary, I have not been able to assure myself, up to this time, that these three bodies can produce any effect. Thus far the effect has been proportionate to the *conducting power* of the substance for electricity. Gold, silver and copper have produced large deflections, lead and tin less. Platina very little. Bismuth and antimony none.

2656. Hence there was every reason to believe that the effects were produced by the currents induced in the mass of the moving metals, and not by any polarity of their particles. I proceeded therefore to test this idea by different conditions of the cores and the apparatus.

2657. In the first place, if produced by induced currents, the great proportion of these would exist in the part of the core near to the dominant magnet, and but little in the more distant parts; whereas in a substance like iron, the polarity which the whole assumes makes length a more important element. I therefore shortened the core of copper from 5½ inches (2643.) to 2 inches, and found the effect not sensibly diminished; even when 1 inch long it was little less than before. On the contrary, when a fine iron wire, 5½ inches in length, was used as core, its effects were strong; when the length was reduced to 2 inches, they were greatly diminished; and again, with a length of 1 inch, still further greatly reduced. It is not difficult to construct a core of copper, with a fine iron wire in its axis, so that when above a certain length it should produce the effects of iron, and beneath that length the effects of copper.

2658. In the next place, if the effect were produced by induced currents in the mass (2642.), division of the mass would stop these currents and so alter the effect; whereas if produced by a true diamagnetic polarity, division of the mass would not affect the polarity seriously, or in its essential nature (2430.). Some copper filings were therefore digested for a few days in dilute sulphuric acid to remove any adhering iron, then well-washed and dried, and afterwards warmed and stirred in the air, until it was seen by the orange colour that a very thin film of oxide had formed upon them: they were finally introduced into a glass tube (2653.) and employed as a core. It produced no effect whatever, but was now as inactive as bismuth.

2659. The copper may however be divided so as either to interfere with the assumed currents or not, at pleasure. Fine copper wire was cut up into lengths of $5\frac{1}{2}$ inches, and as many of these associated together as would form a compact cylinder three-quarters of an inch in diameter (2643.); it produced no effect at the galvanometer. Another copper core was prepared by associating together many discs of thin copper plate, three-quarters of an inch in diameter, and this affected the galvanometer, holding its needle 25° or 30° from zero.

2660. I made a solid helix cylinder, three-quarters of an inch in diameter and 2 inches long, of covered copper wire, one-sixteenth of an inch thick, and employed this as the experimental core. When the two ends of its wire were unconnected, there was no effect upon the experimental helix, and consequently none at the galvanometer; but when the ends were soldered together, the needle was well affected. In the first condition, the currents, which tended to be formed in the mass of moving metal, could not exist because the metal circuit was interrupted; in the second they could, because the circuit was not interrupted; and such division as remained did not interfere to prevent the currents.

2661. The same results were obtained with other metals. A core cylinder of gold, made of half-sovereigns, was very powerful in its effect on the galvanometer. A cylinder of silver, made of sixpenny pieces, was very effectual; but a cylinder made of precipitated silver, pressed into a glass tube as closely as possible, gave no indications of action whatever. The same results were obtained with disc cylinders of tin and lead, the effects being proportionate to the condition of tin and lead as bad conductors (2655.).

2662. When iron was divided, the effects were exactly the reverse in kind. It was necessary to use a much coarser galvanometer and apparatus for the purpose; but that being done, the employment of a solid iron core, and of another of the same size or weight formed of lengths of fine iron wire (2659.), showed that the division had occasioned no inferiority in the latter. The excellent experimental researches of Dove * on the electricity of induction, will show that this ought to be the case.

2663. Hence the result of division in the diamagnetic metals is altogether of a nature to confirm the conclusion, that the effects produced by them are due to in-

* Taylor's Scientific Memoirs, v. p. 129. I do not see a date to the paper.

duced currents moving through their masses, and not to any polarity correspondent in its general nature (though opposed in its direction) to that of iron.

2664. In the third place (2656.), another and very important distinction in the actions of a diamagnetic metal may be experimentally established according as they may be due either to a true polarity, or merely to the presence of temporary induced currents; and as for the consideration of this point diamagnetic and magnetic polarity are the same, the point may best be considered, at present, in relation to iron.

2665. If a core of any kind be advanced towards the dominant magnet and withdrawn from it by a motion of uniform velocity, then a complete journey or *to* and *from* action might be divided into four parts; the *to*, the *stop* after it; the *from*, and the *stop* succeeding that. If a core of iron make this journey, its end towards the dominant magnet becomes a pole, rising in force until at the nearest distance, and falling in force until at the greatest distance. Both this effect, and its *progression* inwards and outwards, cause currents to be induced in the surrounding helix, and these currents are in one direction as the core advances, and in the contrary direction as it recedes. In reality, however, the iron does not travel with a constant velocity; for, because of the communication of motion from a revolving crank at the machine (2643.), it, in the *to* part of the journey, gradually rises from a state of rest to a maximum velocity, which is half-way, and then as gradually sinks to rest again near the magnet:—and the *from* part of the journey undergoes the same variations. Now as the maximum effect upon the surrounding experimental helix depends upon the velocity conjointly with the intensity of the magnetic force in the end of the core, it is evident that it will not occur with the maximum velocity, which is in the middle of the *to* or *from* motion; nor at the *stop* nearest to the dominant magnet, where the core end has greatest magnetic force, but somewhere between the two. Nevertheless, during the *whole* of the advance, the core will cause a current in the experimental helix in one direction, and during the whole of the recession it will cause a current in the other direction.

2666. If diamagnetic bodies, under the influence of the dominant magnet, assume also a polar state, the difference between them and iron being only that the poles of like names or forces are changed in place (2429. 2430.), then the same kind of action as that described for iron would occur with them; the only difference being, that the two currents produced would be in the reverse direction to those produced by iron.

2667. If a commutator, therefore, were to be arranged to gather up these currents, either in the one case or the other, and send them on to the galvanometer in one consistent current, it should change at the moments of the two *stops* (2665.), and then would perform such duty perfectly. If, on the other hand, the commutator should change at the times of maximum velocity or maximum intensity, or at two other times equidistant either from the one *stop* or from the other, then the parts of the opposite currents intercepted between the changes would exactly neutralize each other, and no final current would be sent on to the galvanometer.

2668. Now the action of the iron is, by experiment, of this nature. If an iron wire be simply introduced or taken out of the experimental helix with different conditions of the commutator, the results are exactly those which have been stated. If the machine be worked with an iron wire core, the commutator changing at the stops (2665.), then the current gathered up and sent on to the galvanometer is a maximum; if the commutator change at the moments of maximum velocity, or at any other pair of moments equidistant from the one stop or the other, then the current at the commutator is a minimum, or 0.

2669. There are two or three precautions which are necessary to the production of a pure result of this kind. In the first place, the iron ought to be soft and not previously in a magnetic state. In the next, an effect of the following kind has to be guarded against. If the iron core be away from the dominant magnet at the beginning of an experiment, then, on working the machine, the galvanometer will be seen to move in one direction for a few moments, and afterwards, notwithstanding the continued action of the machine, will return and gradually take up its place at 0°. If the iron core be at its shortest distance from the dominant magnet at the beginning of the experiment, then the galvanometer needle will move in the contrary direction to that which it took before, but will again settle at 0°. These effects are due to the circumstance, that, when the iron is away from the dominant magnet, it is not in so strong a magnetic state, and when at the nearest to it is in a stronger state, than the *mean* or *average state*, which it acquires during the continuance of an experiment; and that in rising or falling to this average state, it produces two currents in contrary directions, which are made manifest in the experiments described. These existing only for the first moments, do, in their effects at the galvanometer, then appear, producing a vibration which gradually passes away.

2670. One other precaution I ought to specify. Unless the commutator changes accurately at the given points of the journey, a little effect is gathered up at each change, and may give a permanent deflection of the needle in one direction or the other. The tongues of my commutator, being at right angles to the direction of motion and somewhat flexible, dragged a little in the *to* and *from* parts of the journey: in doing this they approximated, though only in a small degree, to that which is the best condition of the commutator for gathering up (and not opposing) the currents; and a deflection to the right or left appeared (2677.). Upon discovering the cause and stiffening the tongues so as to prevent their flexure, the effect disappeared, and the iron was perfectly inactive.

2671. Such therefore are the results with an iron core, and such would be the effects with a copper or bismuth core if they acted by a diamagnetic polarity. Let us now consider what the consequences would be if a copper or bismuth core were to act by currents, induced for the time, in its moving mass, and of the nature of those suspected (2642.). If the copper cylinder moved with uniform velocity (2665.), then currents would exist in it, parallel to its circumference, during the whole time of its

motion; and these would be at their maximum force just before and just after the *to* or inner stop, for then the copper would be in the most intense parts of the magnetic field. The rising current of the copper core for the *in* portion of the journey would produce a current in one direction in the experimental helix, the stopping of the copper and consequent falling of its current would produce in the experimental helix a current contrary to the former; the first instant of motion *outwards* in the core would produce a maximum current in it contrary to its former current, and producing in the experimental helix its inductive result, being a current the same as the last there produced; and then, as the core retreated, its current would fall, and in so doing and by its final stop, would produce a fourth current in the experimental helix, in the same direction as the first.

2672. The four currents produced in the experimental helix alternate by twos, *i. e.* those produced by the falling of the first current in the core and the rising of the second and contrary current, are in one direction. They occur at the instant before and after the stop at the magnet, *i. e.* from the moment of maximum current (in the core) before, to the moment of maximum current after, the stop; and if that stop is momentary, they exist only for that moment, and should during that brief time be gathered up by the commutator. Those produced in the experimental helix during the falling of the second current in the core and the rising of a third current (identical with the first) in the return of the core to the magnet, are also the same in direction, and continue from the beginning of the retreat to the end of the advance (or from maximum to maximum) of the core currents, *i. e.* for almost the whole of the core journey; and these, by its change at the maximum moments, the commutator should take up and send on to the galvanometer.

2673. The motion however of the core is not uniform in velocity, and so, sudden in its change of direction, but, as before said (2665.), is at a maximum as respects velocity in the middle of its approach to and retreat from the dominant magnet; and hence a very important advantage. For its stop may be said to commence immediately after the occurrence of the maximum velocity; and if the lines of magnetic force were equal in position and power there to what they are nearer to the magnet, the contrary currents in the experimental helix would commence at those points of the journey; but, as the core is entering into a more intense part of the field, the current in it still rises though the velocity diminishes, and the consequence is, that the maximum current in it neither occurs at the place of greatest velocity, nor of greatest force, but at a point between the two. This is true both as regards the approach and the recession of the core, the two maxima of the currents occurring at points equidistant from the place of rest near the dominant magnet.

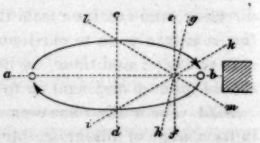
2674. It is therefore at these two points that the commutator should change, if adjusted to produce the greatest effect at the galvanometer by the currents excited in the experimental helix, through the influence of, or in connection with, currents of induction produced in the core; and experiment fully justifies this conclusion.

If the length of the journey from the stop out to the stop in, which is 2 inches (2643. 2644.), be divided into 100 parts, and the dominant magnet be supposed to be on the right-hand, then such an expression as the following, 50|50, may represent the place where the commutator changes, which in this illustration would be midway in the to and from motion, or at the places of greatest velocity.

2675. Upon trial of various adjustments of the commutator, I have found that from 77|23 to 88|12, gave the best result with a copper core. On the whole, and after many experiments, I conclude that with the given strength of electro-magnet, distance of the experimental core when at the nearest from the magnet, length of the whole journey, and average velocity of the machine, 86|14 may represent the points where the induced currents in the core are at a maximum and where the commutator ought to change.

2676. From what has been said before (2667.), it will be seen that both in theory and experiment these are the points in which the effect of any polarity, magnetic or diamagnetic, would be absolutely nothing. Hence the power of submitting by this machine metals and other bodies to experiment, and of eliminating the effects of magnetic polarity, of diamagnetic polarity, and of inductive action, the one from the others: for either by the commutator or by the direction of the polarity, they can be separated; and further, they can also be combined in various ways for the purpose of elucidating their joint and separate action.

2677. For let the arrows in the diagram represent the to and from journey, and the intersections of the lines *a*, *b* or *c*, *d*, &c. the periods in the journey when the commutator changes (in which case *c*, *d* will correspond to 50|50, and *e*, *f* to 86|14), then *a*, *b* will represent the condition of the commutator for the maximum effect of iron or any other polar body. If the line *a*, *b* be gradually revolved until parallel to *c*, *d*, it will in every position indicate points of commutator change, which will give the iron effect at the galvanometer by a deflection of the needle always in the same direction; it is only when the ends *a* and *b* have passed the points *c* and *d*, either above or below, that the direction of the deflection will change for iron. But the line *a*, *b* indicates those points for the commutator with which no effect will be produced on the galvanometer by the induction of *currents* in the mass of the core. If the line be inclined in one direction, as *i*, *k*, then these currents will produce a deflection at the galvanometer on one side; if it be inclined in the other direction, as *l*, *m*, then the deflection will be on the other side. Therefore the effects of these induced currents may be either combined with, or opposed to, the effects of a polarity, whether it be magnetic or diamagnetic.



2678. All the metals before mentioned (2655.), namely, gold, silver, copper, tin, lead, platina, antimony and bismuth, were submitted to the power of the electro-magnet under the best adjustment (2675.) of the commutator. The effects were stronger

than before, being now at a maximum, but in the same order; as regarded antimony and bismuth, they were very small, amounting to not more than half a degree, and may very probably have been due to a remainder of irregular action in some part of the apparatus. All the experiments with the divided cores (2658, &c.) were repeated with the same results as before. Phosphorus, sulphur and gutta percha did not, either in this or in the former state of the commutator, give any indication of effect at the galvanometer.

2679. As an illustration of the manner in which this position of the commutator caused a separation of the effects of copper and iron, I had prepared a copper cylinder core 2 inches in length having an iron wire in its axis, and this being employed in the apparatus gave the pure effect of the copper with its induced currents. Yet this core, as a whole, was highly magnetic to an ordinary test-needle; and when the two changes of the commutator were not equidistant from the one stop or the other (2670. 2677.), the iron effect came out powerfully, overruling the former and producing very strong contrary deflections at the needle. The platinum core which I have used is an imperfect cylinder, 2 inches long and 0·62 of an inch thick: it points magnetically between the poles of a horseshoe electro-magnet (2381.), making a vibration in less than a second, but with the above condition of the commutator (2675.) gives 4° of deflection due to the induced currents, the magnetic effect being annulled or thrown out.

2680. Some of the combined effects produced by oblique position of the commutator points were worked out in confirmation of the former conclusions (2677.). When the commutator was so adjusted as to combine any polar power which the bismuth, as a diamagnetic body, might possess, with any conducting power which would permit the formation of currents by induction in its mass (2676.), still the effects were so minute and uncertain as to oblige me to say that, experimentally, it is without either polar or inductive action.

2681. There is another distinction which may usefully be established between the effects of a true sustainable polarity, either magnetic or diamagnetic, and those of the transient induced currents dependent upon *time*. If we consider the resistance in the circuit, which includes the experimental helix and the galvanometer coil, as nothing, then a magnetic pole of constant strength passed a certain distance into the helix, would produce the same amount of current electricity in it, whether the pole were moved into its place by a quick or a slow motion. Or if the iron core be used (2668.) the same result is produced, provided, in any alternating action, the core is left long enough at the extremities of its journey to acquire, either in its quick or slow alternation, the same state. This I found to be the fact when no commutator nor dominant magnet was used; a single insertion of a weak magnetic pole gave the same deflection, whether introduced quickly or slowly; and when the residual dominant magnet, an iron wire core, and the commutator in its position *a*, *b* (2677.) were used, four journeys to and from produced the *same* effect at the galvanometer when the velocities were as 1 : 5 or even as 1 : 10.

2682. When a copper, silver, or gold core is employed in place of the iron, the effect is very different. There is no reason to doubt, that, as regards the core itself, the same amount of electricity is thrown into the form of induced circulating currents within it, by a journey to or from, whether that journey is performed quickly or slowly: the above experiment (2681.) in fact confirms such a conclusion. But the effect which is produced upon the experimental helix is not proportionate to the whole amount of these currents, but to the maximum intensities to which they rise. When the core moves slowly, this intensity is small; when it moves rapidly, it is great, and necessarily so, for the same current of electricity has to travel in the two differing periods of time occupied by the journeys. Hence the quickly moving core should produce a far higher effect on the experimental helix than the slowly moving core; and this also I found to be the fact.

2683. The short copper core was adjusted to the apparatus, and the machine worked with its average velocity until forty journeys to and from had been completed; the galvanometer needle passed 39° west. Then the machine was worked with a greater rapidity, also for forty journeys, and the needle passed through 80° or more west; finally, being worked at a slow rate for the same number of journeys, the needle went through only 21° west. The extreme velocities in this experiment were probably as 1 : 6; the time in the longest case was considerably less than that of one vibration of the needle (2651.), so that I believe all the force in the slowest case was collected. The needle is very little influenced by the swing or momentum of its parts, because of the deadening effect of the copper plate beneath it, and, except to return to zero, moves very little after the motion of the apparatus ceases. A silver core produced the same results.

2684. These effects of induced currents have a relation to the phenomena of revulsion which I formerly described (2310. 2315. 2338.), being the same in their exciting cause and principles of action, and so the two sets of phenomena confirm and illustrate each other. That the revulsive phenomena are produced by induced currents, has been shown before (2327. 2329. 2336. 2339.); the only difference is, that with them the induced currents were produced by exalting the force of a magnet placed at a fixed distance from the affected metal; whilst in the present phenomena, the force of the magnet does not change, but its distance from the piece of metal does.

2685. So also the same circumstances which affect the phenomena here affect the revulsive phenomena. A plate of metal will, as a whole, be well-revulsed; but if it be divided across the course of the induced currents it is not then affected (2529.). A ring helix of copper wire, if the extremities be unconnected, will not exhibit the phenomena, but if they be connected then it presents them (2660.).

2686. On the whole, the revulsive phenomena are a far better test and indication of these currents than the present effects; especially if advantage be taken of the division of the mass into plates, so as to be analogous, or rather superior, in their action to the disc cylinder cores (2659. 2661.). Platinum, palladium and lead in leaf or foil, if cut or folded into squares half an inch in the side, and then packed regularly

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together, will show the phenomena of revulsion very well; and that according to the direction of the leaves, and not of the external form. Gold, silver, tin and copper have the revulsive effects thus greatly exalted. Antimony, as I have already shown, exhibits the effect well (2514. 2519.). Both it and bismuth can be made to give evidence of the induced currents produced in them when they are used in thin plates, either single or associated, although, to avoid the influence of the diamagnetic force, a little attention is required to the moments of making and breaking contact between the voltaic battery and the electro-magnet.

2687. Copper, when thus divided into plates, had its revulsive phenomena raised to a degree that I had not before observed. A piece of copper foil was annealed and tarnished by heat, and then folded up into a small square block, half an inch in the side and a quarter of an inch thick, containing seventy-two folds of the metal. This block was suspended by a silk film as before (2248.), and whilst at an angle of 30° or thereabouts with the equatorial line (2252.), the electro-magnet was excited; it immediately advanced or turned until the angle was about 45° or 50°, and then stood still. Upon the interruption of the electric current at the magnet the revulsion came on very strongly, and the block turned back again, passed the equatorial line, and proceeded on until it formed an angle of 50° or 60° on the other side; but instead of continuing to revolve in that direction as before (2315.), it then returned on its course, again passed the equatorial line, and almost reached the axial position before it stood still. In fact, as a mass, it vibrated to and fro about the equatorial line.

2688. This however is a simple result of the principles of action formerly developed (2329. 2336.). The revulsion is due to the production of induced currents in the suspended mass during the falling of the magnetism of the electro-magnet; and the effect of the action is to bring the axis of these induced currents parallel to the axis of force in the magnetic field. Consequently, if the time of the fall of magnetic force, and therefore of the currents dependent thereon, be greater than the time occupied by the revulsion of the copper block as far as the equatorial line, any further motion of it by momentum will be counteracted by a contrary force; and if this force be strong enough the block will return. The conducting power of the copper and its division into laminæ, tend to set up these currents very readily and with extra power; and the very power which they possess tends to make the time of a vibration so short, that two or even three vibrations can occur before the force of the electro-magnet has ceased to fall any further. The effect of *time*, both in the rising and falling of power, has been referred to on many former occasions (2170. 2650.), and is very beautifully seen here.

2689. Returning to the subject of the assumed polarity of bismuth, I may and ought to refer to an experiment made by Reich, and described by Weber*, which, if

* Taylor's Scientific Memoirs, v. p. 480.

I understand the instruction aright, is as follows: a strong horseshoe magnet is laid upon a table in such a position that the line joining its two poles is perpendicular to the magnetic meridian and to be considered as prolonged on one side; in that line, and near the magnet, is to be placed a small powerful magnetic needle, suspended by cocoon silk, and on the other side of it, the pole of a bar magnet, in such a position and so near, as exactly to counteract the effect of the horseshoe magnet, and leave the needle to point exactly as if both magnets were away. Then a mass of bismuth being placed between the poles of the horseshoe magnet is said to react upon the small magnet needle, causing its deflection in a particular direction, and this is supposed to indicate the polarity of the bismuth under the circumstances, as it has no such action when the magnets are away. A piece of iron in place of the bismuth produces the contrary deflection of the needle.

2690. I have repeated this experiment most anxiously and carefully, but have never obtained the slightest trace of action with the bismuth. I have obtained action with the iron; but in those cases the action was far less than if the iron were applied outside between the horseshoe magnet and the needle, or to the needle alone, the magnets being entirely away. On using a garnet, or a weak magnetic substance of any kind, I cannot find that the arrangement is at all comparable for readiness of indication or delicacy, with the use of a common or an astatic needle, and therefore I do not understand how it could become a test of the polarity of bismuth when these fail to show it. Still I may have made some mistake; but neither by close reference to the description, nor to the principles of polar action, can I discover where.

2691. There is an experiment which PLÜCKER described to me, and which at first seems to indicate strongly the polarity of bismuth. If a bar of bismuth (or phosphorus) be suspended horizontally between the poles of the electro-magnet, it will go to the equatorial position with a certain force, passing, as I have said, from stronger to weaker places of action (2267.). If a bar of iron of the same size be fixed in the equatorial position a little below the plane in which the diamagnetic bar is moving, the latter will proceed to the equatorial position with much greater force than before, and this is considered as due to the circumstance, that, on the side where the iron has N polarity, the diamagnetic body has S polarity, and that on the other side the S polarity of the iron and the N polarity of the bismuth also coincide.

2692. It is however very evident that the lines of magnetic force have been altered sufficiently in their intensity of direction, by the presence of the iron, to account fully for the increased effect. For, consider the bar as just leaving the axial position and going to the equatorial position; at the moment of starting its extremities are in places of stronger magnetic force than before, for it cannot be doubted for a moment that the iron bar determines more force from pole to pole of the electro-magnet than if it were away. On the other hand, when it has attained the equatorial position, the extremities are under a much weaker magnetic force than they were subject to in the *same places* before; for the iron bar determines downwards upon itself much

of that force, which, when it is not there, exists in the plane occupied by the bismuth. Hence, in passing through 90°, the diamagnetic is urged by a much greater difference of intensity of force when the iron is present than when it is away; and hence, probably, the whole additional result. The effect is like many others which I have referred to in magnecrystallic action (2487–2497.), and does not, I think, add anything to the experimental proof of diamagnetic polarity.

2693. Finally, I am obliged to say that I can find no experimental evidence to support the hypothetical view of diamagnetic polarity (2640.), either in my own experiments, or in the repetition of those of WEBER, REICH, or others I do not say that such a polarity does not exist; and I should think it possible that WEBER, by far more delicate apparatus than mine, had obtained a trace of it, were it not that then also he would have certainly met with the far more powerful effects produced by copper, gold, silver, and the better conducting diamagnetics. If bismuth should be found to give any effect, it must be checked and distinguished by reference to the position of the commutator, division of the mass by pulverization, influence of time, &c. It appears to me also, that, as the magnetic polarity conferred by iron or nickel in very small quantity, and in unfavourable states, is far more readily indicated by its effect on an astatic needle, or by pointing between the poles of a strong horseshoe magnet, than by any such arrangement as mine or WEBER's or REICH's, so diamagnetic polarity would be much more easily distinguished in the same way, and that no indication of that polarity has as yet reached to the force and value of those already given by BRUGMANN and myself.

2694. So, at present, the actions represented or typified by iron, by copper and by bismuth, remain distinct; and their relations are only in part made known to us. It cannot be doubted that a larger and simpler law of action than any we are yet acquainted with, will hereafter be discovered, which shall include all these actions at once; and the beauty of WEBER's suggestion in this respect was the chief inducement to me to endeavour to establish it.

2695. Though from the considerations above expressed (2693.) I had little hopes of any useful results, yet I thought it right to submit certain magnecrystallic cores to the action of the apparatus. One core was a large group of symmetrically disposed crystals of bismuth (2457.); another a very large crystal of red ferroprussiate of potassa; a third a crystal of calcareous spar; and a fourth and fifth large crystals of protosulphate of iron. These were formed into cylinders of which the first and fourth had the magnecrystallic axes (2479.) parallel to the axis of the cylinder, and the second, third and fifth, had the equatorial direction of force (2594. 2595. 2596.) parallel to the axis of the cylinder. None of them gave any effect at the galvanometer, except the fourth and fifth, and these were alike in their results, and were dependent for them on their ordinary magnetic property.

2696. Some of the expressions I have used may seem to imply, that, when employing the copper and other cores, I imagine that currents are first induced in them by the

dominant magnet, and that these induce the currents which are observed in the experimental helix. Whether the cores act directly on the experimental helix or indirectly through their influence on the dominant magnet, is a very interesting question, and I have found it difficult to select expressions, though I wished to do so, which should not in some degree prejudge that question. It seems to me probable, that the cores act indirectly on the helix, and that their immediate action is altogether directed towards the dominant magnet, which, whether they consist of magnetic or diamagnetic metals, raises them into power either permanently or transiently, and has their power for that time directed towards it. Before the core moves to approach the magnet, the magnet and experimental helix are in close relation; and the latter is situated in the intense field of magnetic force which belongs to the pole of the former. If the core be iron, as it approaches the magnet it causes a strong convergence and concentration of the lines of magnetic force upon itself; and these, as they so converge, passing through the helix and across its convolutions, are competent to produce the currents in it which are obtained (2653. 2668.). As the iron retreats these lines of force diverge, and again crossing the line of the wire in the helix in a contrary direction to their former course, produce a contrary current. It does not seem necessary, in viewing the action of the iron core, to suppose any direct action of it on the helix, or any other action than this which it exerts upon the lines of force of the magnet. In such a case its action upon the helix would be indirect.

2697. Then, by all parity of reasoning, when a copper core enters the helix its action upon it should be indirect also. For the currents which are produced in it are caused by the direct influence of the magnet, and must react equivalently upon it. This they do, and because of their direction and known action, they will cause the lines of force of the magnet to diverge. As the core diminishes in its velocity of motion, or comes to rest, the currents in it will cease, and then the lines of force will converge; and this divergence and convergence, or passage in two directions across the wire of the experimental helix, is sufficient to produce the two currents which are obtained in the advance of the core towards the dominant magnet (2671. 2673.). A corresponding effect in the contrary direction is produced by the retreat of the core.

2698. On the idea that the actions of the core were not of this kind, but more directly upon the helix, I interposed substances between the core and the helix during the times of the experiment. A thick copper cylinder 2·2 inches long, 0·7 of an inch external diameter, and 0·1 of an inch internal diameter, and consequently 0·3 of an inch thick in the sides, was placed in the experimental helix, and an iron wire core (2668.) used in the apparatus. Still, whatever the form of the experiment, the kind and amount of effect produced were the same as if the copper were away, and either glass or air in its place. When the dominant magnet was removed and the wire core made a magnet, the same results were produced.

2699. Another copper lining, being a cylinder 2·5 inches long, 1 inch in external

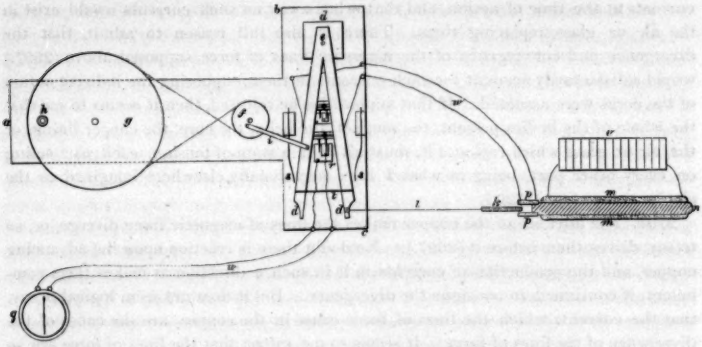
diameter, and one-eighth of an inch in thickness, was placed in the experimental helix, and cores of silver and copper five-eighths of an inch in thickness, employed as before, with the best condition of the commutator (2675.): the effects, with and without the copper, or with and without the glass, were absolutely the same (2698.).

2700. There can be no doubt that the copper linings, when in place, were full of currents at the time of action, and that when away no such currents would exist in the air or glass replacing them. There is also full reason to admit, that the divergence and convergence of the magnetic lines of force supposed above (2697.) would satisfactorily account for such currents in them, supposing the indirect action of the cores were assumed. If that supposition be rejected, then it seems to me that the whole of the bodies present, the magnet, the helix, the core, the copper lining, or the air or glass which replaces it, must all be in a state of tension, each part acting on every other part, being in what I have occasionally elsewhere imagined as the electro-tonic state (1729.).

2701. The advance of the copper makes the lines of magnetic force diverge, or, so to say, drives them before it (2697.). No doubt there is reaction upon the advancing copper, and the production of currents in it in such a direction as makes them competent, if continued, to continue the divergence. But it does not seem logical to say, that the currents which the lines of force cause in the copper, are the cause of the divergence of the lines of force. It seems to me, rather, that the lines of force are, so to say, diverged, or bent outward by the advancing copper (or by a connected wire moving across lines of force in any other form of the experiments), and that the reaction of the lines of force upon the forces in the particles of the copper cause them to be resolved into a current, by which the resistance is discharged and removed, and the line of force returns to its place. I attach no other meaning to the words *line of force* than that which I have given on a former occasion (2149.).

Royal Institution,
14 *Dec.* 1849.

Plan of the Apparatus employed in Dr. FARADAY's Researches, Series XXIII. p. 172.



a, *b*, *c* frame board; *d*, *d*, *d* wooden lever, of which *e* is the axis, *f* the crank-wheel, and *g* the great wheel with its handle *h*; *i* the bar connecting the crank-wheel and lever; *k* a cylinder or core of metal to be submitted to experiment; *l* the rod connecting it with the lever; *m* the helix of the electro-magnet; *n* the iron core, and *o* the exciting battery; *p* the experimental helix; *q* the galvanometer, 20 feet from the electro-magnet; *r* the commutator; *w*, *w* connecting wires; *s*, *s* springs of brass or copper; *t* a copper rod connecting the two arms of the lever, to give strength. The plan is to a scale of one-fifteenth: the part at the electro-magnet and experimental helix is in section; the further description is in paragraphs 2643, 2644, 2645 and 2648 of the Experimental Researches.

VIII. *On the Development of the Retina and Optic Nerve, and of the Membranous Labyrinth and Auditory Nerve.* *By* HENRY GRAY, *M.R.C.S. Communicated by* W. BOWMAN, *F.R.S., Professor of Physiology and of General and Morbid Anatomy in King's College, London.*

Received October 18, 1849,—Read January 31, 1850.

THE following observations, which I have ventured to offer to the Royal Society, are intended to demonstrate the mode of evolution of the essential parts of the visual and auditory apparatus.

In the first part I have considered the mode of development of the optic nerve and retina, and also of the various layers of this membrane. In the second part, I have traced the evolution of the membranous labyrinth and auditory nerve. Many of these observations have not (as far as I am acquainted) been previously made, at the same time they will, I think, confirm in a remarkable manner the account that has already been given of the structure of these parts*.

In the minute and accurate account of the structure of the retina which Mr. BOWMAN has lately given in a series of lectures on the Anatomy of the Eye, he has shown that this essential part of the visual organ "is a nervous sheet containing nearly all the structural elements that are found in any part of the nervous system, consisting of an unbroken sheet of gray nervous matter, continuous by its fibrous internal surface with the axes of the tubules of the optic nerve, and having its external surface formed by a structure similar to that of the cineritious substance of the cerebral hemispheres. Its permeation by a close network of capillaries assimilates it still further to the gray nervous matter, for which reasons it may be considered as a portion of the cerebrum advanced towards the surface of the body in a suitable relation to a dioptric apparatus for the reception of rays of light from external objects."

The following observations are intended to demonstrate the evolution and mode of development of this membrane in the embryo chick, and they will, I think, confirm in a most striking manner the account that has been given of the structure of this part.

It is not until the thirty-third hour of incubation that there is any indication of the evolution of the retina or of the rudimentary eye. At the thirty-first hour (Plate VIII. fig. 1) the cephalic extremity of the embryo is indicated by its presenting a somewhat

* Some of the observations on the development of the retina may be found in my Prize Essay "On the Anatomy and Physiology of the Nerves of the Human Eye," contained in the Library of the Royal College of Surgeons, but unpublished.

dilated end, but no protrusion can be observed in the situation where the eye is to be subsequently formed. At the thirty-third hour (fig. 2) there is observed on each side of the cephalic extremity a protrusion of its walls, which at the thirty-sixth hour (fig. 3) has very much increased, having become more elongated and protruded outwards, presenting a somewhat dilated end, and being slightly constricted at its connection with the cerebral cell from which it arises; the whole embryo is enlarged, and now there is a distinct division of the brain into its several primitive cells; this protrusion, which is well represented in fig. 3, is the first distinct indication of the mode of development of this membrane.

In an embryo chick, examined at the forty-sixth hour of incubation from the cerebral aspect (figs. 4 and 5), the future brain consisted of several cells; the anterior, which was the largest, corresponded to the cerebral lobes; the middle, smaller in size, to the future optic lobes; and the posterior, the smallest, but most elongated, to the medulla oblongata. From the most anterior one there arose a protrusion on each side, having a somewhat dilated extremity: this protrusion I will call the optic vesicle. The cavity of the cerebral cell from which it arose was very distinct and its wall clear and pellucid, and appeared to communicate with the optic vesicle, which was also hollow.

As the cavity of the cerebral cell passed outwards on both sides into the optic vesicle it became less distinct, as there the wall of the vesicle, which is darkly granular, makes it in this situation less apparent, whilst the cavity in the cerebral cell itself was distinctly seen from the thinness of its wall on its ventral aspect. If the embryo is examined from its dorsal surface (its natural position in the egg), the cerebral cell presents an external convex surface, whilst projecting from each side are seen the optic vesicles. The cavity of the cell and its communication with the optic vesicle, cannot on this surface be distinctly demonstrated on account of its wall being thicker than on the ventral side. The optic vesicle is bounded externally by a well-defined line which lines the outer surface of the protrusion, and seems to be connected with the envelopes of the cerebral mass; this is again bounded by the tegumentary layer of the embryo. When examined with a high magnifying power, the vesicle presented a pale granular texture without any indication of cellular structure. This description of the origin of the retina, although confirmed by similar observations, described by Baer in the Encyclopédie Anatomique, tom. viii., is not in accordance with that of some other celebrated physiologists. According to Wagner, the protrusion which forms the future retina arises from the middle and anterior cerebral cells, whilst Huschke describes it as "a simple rudiment, consisting of a fosette; that the dorsal laminæ form in front of their anterior dilatation, the first cerebral cell ultimately dividing this into two lateral halves, from which result the two rudimentary eyes." He says also that this fosette is formed before the end of the first day. From many observations I have made I could never see what these observers have described, and, coinciding as my observations do so exactly with those of Baer, the conclusions which I have stated regarding the origin of this membrane would seem

to be thereby confirmed. On examining a chick nine hours after this period, that is, at the fifty-fifth hour of incubation (fig. 6), the cavity before so distinctly seen in the anterior cerebral cell was much less apparent; the walls of the cell have also much increased in size, not only projecting upwards but laterally, so as partly to cover over the inner portion of the protruded optic vesicle, which at the second day was so distinctly seen; the head had also become more curved, which rendered a good examination of the eye somewhat difficult. On manipulating the specimen so as to obtain a view from above downwards, the embryo lying on its ventral surface, the outer portion of the protruded vesicle was distinctly seen bounded by a clear defined inner border and an outer paler one; the dark inner one was lost in the dark granular mass, which by its circular form indicated the rudimentary eye; the outer layer was the external tegumentary membrane of the embryo. At the sixty-second hour (Plate IX. fig. 8) the optic vesicle is seen to be apparently situated between the anterior and middle cerebral cells; this I believe depends on the great increase of development of these cells, and the curved form which the head now assumes, making its apparent origin to be from both, as stated by Wagner. On carefully examining it, the exterior dark line was beautifully defined all around, and presented the appearance of an outer covering to the eyeball; in this apparent cavity was seen a pyriform vesicle, the future retina, presenting a distinct outline, except at its inner side, where it became constricted and of a tubular form, and to all appearance was continuous with the cerebral mass; this constricted portion, the tubular end, I suppose to be the optic nerve, the dilated portion the retina. Internal to the retina was the circular crystalline lens, with its central but indistinct nucleus. The conclusions I have come to, from the observations made on the specimens from which the drawings 5, 6 and 8 are taken, are quite at variance with those of Huschke. He says that between the second and third days the two layers of the retina are formed in the following manner. He describes the capsule of the lens as being an inverted portion of the common integument, which pushes inwards the dilated end of the optic vesicle, and thus forms a double layer; the outer one he describes as Jacob's membrane, the inner inverted one the true retina. In order to ascertain the correctness of this statement, I examined the eye at four successive periods between the second and third days, at the forty-eighth, fifty-fifth, sixty-second and seventy-second hours. I not only examined them laterally, as they naturally presented themselves on removing them from the egg, but both on their dorsal and ventral aspect; and if the lens had been, as he described, an inversion of the integument pressing in the dilated end of the optic vesicle, both of the latter positions would have been most favourable for demonstrating it. The lens is however formed in quite a different manner; it is first seen as a rather ill-defined granular mass in the cavity of the vesicle itself, containing in its centre a nucleus: this is seen on the first half of the third day. On the third it becomes more distinct, a well-defined line now bounds its margin; between the fourth and fifth days, the granules become darker and more aggregated towards the centre, leaving a space

bounded by a dark outer line; this is now the capsule of the lens, the inner one the bounding margin of the lens itself. Nor could I ever see satisfactorily any doubling-in of the retina so as to form two layers, for in no position that I put the embryo, in each of the several examinations that I made, could I ever detect but a single layer; and besides, as I shall show hereafter, Jacob's membrane is not developed until a much later period. I cannot forbear here adding the conclusions Bischoff has come to from his observations on this point. Although many anatomists of great reputation follow the opinion of Huschke, he says, "Malgré ces autorités je dois avouer qu'il m'a été impossible même chez de très jeunes embryons de chien, de lapin, et de rat, d'apercevoir sur la face antérieure de l'œil aucune trace d'une semblable intromission des téguments extérieurs, quoique dans certains cas, je sois resté incertain de savoir s'il existait déjà une capsule cristalline et un cristallin*."

At the seventieth hour (fig. 7) the circular outline of the eyeball has become quite distinct, not only externally, but now the line may be traced internally, where previously it was only indicated by the dark circular granular mass, the forming eyeball. The lens is also more distinctly seen bounded by its well-defined circular border, indicating its forming capsule, and the nucleus in its centre is plainly visible. When examined on its under surface, the embryo lying on its dorsal aspect, the original protrusion is seen to have become still more pyriform in shape and more constricted at its inner part, so that the more dilated portion now clearly resembles the future retina, the constricted and tubular portion the optic nerve; the more gradual contraction of this protrusion and separation of it from the cerebral mass is also now more clearly seen. The cavity, which on the second day existed in the cerebral cell and communicated with the protrusion, is now closed in, with the exception of a distinct fissure, which, commencing by curved borders at the margin of the lens, was seen to be continued inwards in the direction of the cerebral mass through the tubular portion of the protrusion, the optic nerve.

The fissure seems to be evidently connected (as Bischoff also supposes) with the separation which is effected between the ocular vesicle and the pedicle by which it is connected with the cerebral cell, the fissure at first being wide and extending as far as the anterior part of the eye, at its inferior and inner side; but as the tubular portion of the protrusion becomes more solidified and converted into the true optic nerve, the fissure becomes much narrowed. No doubt this is analogous to the fissure which exists permanently in the retina and optic nerve in Fishes, as is seen in the Cod. In the Turtle the fissure exists in the nerve though not in the retina, whilst in Birds it appears to be the same slit which is here described, through which the pecten gains admission into the interior of the eye.

On the first half of the fourth day (fig. 9) the whole organ seems to be increased in size: the exterior lamina was distinctly continuous all round, and was of a dark granular texture; the second layer the retina presented a different appearance to

* Anatomie Encyclopédie, tom. viii. p. 324.

what was seen on the third day; it had become more spherical in shape and increased in size; it now appeared to commence at the margin of the lens, which was situated at the more anterior part of the eye; it could not be traced around it, as in some of the preceding observations, but only overlapped it slightly by a thin beveled border, so that it appeared that the most external part of the original protruded vesicle had become absorbed to complete the formation of this rapidly developing membrane. The tubular portion of the original protrusion (the optic nerve), from the great development of the cerebral mass, was hidden from view.

On the fourth day (fig. 10) the eye had become more spherical in form, the outer envelope was distinct and darkly granular; it appeared now to terminate at the edge of the lens, whilst a paler line could be traced over this body, an evident indication of the formation of the sclerotic and cornea. The retina was now less distinctly marked on account of the dark granular tinge beneath the outer envelope; from the formation of the pigment in the epithelial cells of the choroid, it could now only be traced to the edge of the lens, not overlapping it as in the last examination: a distinct fissure was still perceptible on the under surface.

On the fifth day (fig. 11) the eye had greatly increased in size; and along its under surface the fissure was seen running, from its anterior part at the margin of the lens, to a line which bordered the back part of the sclerotic; the capsule of the lens was distinctly formed and separate from the lens itself. Both optic nerves were seen; they were tubular in form and presented a pale granular appearance; they passed inwards in the direction of the under surface of the corpora quadrigemina, but they were not united together in the chiasma until the seventh day. At this period, on making a vertical section of the organ, the retina was to the naked eye distinctly observed to arise from the margin of the lens, and could be detached from the other membranes as a perfectly distinct and separate layer.

From these observations it is seen that the retina is originally a protrusion from the anterior cerebral cell, being hollow and communicating with its cavity; that as the progressive development of the brain takes place, the optic vesicle becomes more separated from its parent cell and assumes a pyriform shape, presenting a dilated extremity, the future retina, and a tubular portion (the optic nerve). In progress of development a fissure is observed on its under surface, which is evidently connected with the separation which is effected between the ocular vesicle and the tubular pedicle (the optic nerve) which connects it with the cerebral cell. As this tubular prolongation becomes solidified so as to form the optic nerve, no communication can be traced between the optic vesicle and the cavity, from which it is an offset. By degrees the spherical end of the protrusion is absorbed, and the retina, now fully formed, becomes attached to the margin of the lens, having previously completely surrounded that body. The optic nerve can then be seen not only to be connected to the anterior cerebral cell, but uniting with its fellow at the under surface of the optic lobes, is seen partly to terminate in those bodies.

I shall proceed, in the next place, to consider the development of the various layers of the retina.

Structure of the Retina of the Chick at the Eighth Day of Incubation.

The retina may at this period be distinctly separated as a thin transparent layer from the other membranes. Its choroidal surface appears to be composed of a closely aggregated mass of globular nuclei; these bodies are about the size of the red corpuscles of the blood, and form about one-half of the entire thickness of the membrane; they apparently correspond to the "agglomerated granules" mentioned by Bowman as forming a considerable portion of the membrane in the normal state; they are highly refractive and of a slight yellow tinge. The deep surface of the membrane consists of some fine granular matter, and a mass of pale and exceedingly delicate nucleated cells, precisely similar to those surrounding the meshes of the fibrous lamina in the normal structure of the membrane. No trace at this period existed of either the membrana Jacobi, or the fibrous lamina of the retina.

On the Development of the Membrana Jacobi.

Between the thirteenth and fourteenth days the choroidal surface of the retina presents an exceedingly fine pale granular stratum, which covers in the "agglomerated granular mass" beneath. On the fifteenth day numerous exceedingly minute and highly refractive yellowish granules are imbedded in it; they vary in size, between the 5000th and the 8000th part of an inch in diameter, and around some of these a fine delicate cell-wall can be traced; if a good view can now be obtained of this surface, it will present the appearance of a delicate epithelial layer. This I believe to be the first stage in the development of Jacob's membrane; for on the eighteenth day the cells, which were previously of a circular form, had now become elongated, some being of an oval shape, whilst in others the almost perfect rod-like body was formed; they now lie in a slightly imbricated manner, and their nuclei, which are of a bright yellow colour, are placed at the apices of the rods; in some cases however they occupy the middle of these bodies; their deep ends are larger than their choroidal ends, and are strongly attached by this surface to the "agglomerated granular layer" beneath; so intimate is their connexion that it is difficult to get a good view of a single rod in the field whilst examining them, probably on account of their perfect separation from this layer not having yet taken place. On the twenty-first day Jacob's membrane is similar to what is seen in the full-grown bird; the rods are now closely packed together, standing perpendicularly upwards, and all of an elongated cylindrical form, their tips being occupied by the brilliant yellow bodies before noticed.

On the Development of the Fibrous Lamina.

The first trace of the fibrous lamina is seen between the fourteenth and fifteenth days: on examining the deep surface of the retina at this period, it is seen to be com-

posed of a very fine pale granular lamina, marked by numerous faint longitudinal striæ: on the eighteenth, this lamina, when separated from the rest of the membrane, is composed of numerous fibrillated bundles, which interlacing with each other form numerous meshes, in which are deposited the gray nucleated vesicles, which are seen to be formed as early as the eighth day. On the twenty-first day this lamina presents the same structure as is found in the full-grown bird. The preceding observations can, I think, be applied in explanation of some lately disputed points in connection with the anatomy and physiology of the retina and optic nerve. And first of the retina.

This membrane has been seen to arise as a protrusion from the cells forming the future brain. Now in the microscopic anatomy of this membrane, as described by Bowman, the vesicular layer of the retina is stated to be analogous to the vesicular layer of the hemisphere of the brain, whilst Henle, and other anatomists of great note, consider the elements of this layer to be more analogous to epithelium. From the circumstance of the retina arising, as it undoubtedly does, from the cerebral cells, being in fact part of them and performing a similar function, we have, I think, a great proof of the similarity in the structure of these two parts. There is another point also, I think, of some importance in proving, as it does, that the opinion of some modern anatomists is incorrect in stating that none of the fibres of the optic nerve can be traced to the optic thalamus. I have said that the origin of the retina is from the anterior cerebral cell, and that at a future period the optic nerve could be traced uniting with its fellow of the opposite side beneath the optic lobes. It is in the anterior cerebral cell that the thalami are subsequently formed, which makes it exceedingly probable that some of its fibres are connected with it, although the greater majority may be traced to the optic lobes.

These facts I think are of some importance, and prove how deductions formed from microscopic embryology may be applied to confirm dissections or microscopic investigations made on the same parts in the mature animal.

On the Development of the Membranous Labyrinth and Auditory Nerve.

The observations I made prior to my description of the mode of evolution of the retina will almost apply here as a preface to my observations on the development of the membranous labyrinth and auditory nerve, for the essential part of this membrane consists, like the retina, of a fibrous lamina formed of the terminal axes, cylinders of the nerve tubules or of terminal loops of nerves, which are in intimate relation with a layer of dark and closely-set nucleated cells, not unlike those found lying between the meshes of the fibrous lamina of the retina; like it also, it may be regarded (as the following observations will show) as a protruded portion of the brain, modified somewhat in its texture and connected with an appropriate apparatus, which receives and transmits its peculiar impressions.

The following observations are intended to demonstrate the mode of development of this membrane, and they will, I think, confirm, not only the description given of

the structure of this part, but show the striking analogy which exists between it and the retinal expansion.

At present two opinions exist regarding the evolution of the ear-bulb. It is stated by Baer that it arises soon after the appearance of the eye, in the form of a tubular prolongation of the brain, which is hollow, and communicates with the cavity of the fourth ventricle, its peripheral extremity forming a vesicular dilatation, which is gradually separated from the brain. Into this vesicle, which is the analogue of the labyrinth, there is protruded inwards a reflection of the integument, which forms all the accessory parts of the organ of hearing. Huschke's account is entirely different; he says that the membranous labyrinth does not arise from the brain, but is originally a blind sac of the skin with an excretory duct, which gradually contracting, is at last separated from the common integument and exists as a separate sac beneath it. The following observations coincide partly with the description given by Baer; at the same time I shall venture to state some facts in connection with this point that have not been (as far as I am acquainted) previously noticed. In the embryo chick at the fiftieth hour, soon after the close of the second day, I observed that the medulla oblongata was not closed in above, but presented a large open shallow cavity, the analogue of the fourth ventricle. At the cephalic extremity it communicated with the optic lobes and the anterior cerebral cell by means of a small circular orifice. From the central part of the wall of this cavity, and exactly opposite to the second branchial cleft, the first rudiment of the auditory sac was visible, in the form of a small protruded vesicle of a somewhat flattened circular shape; this vesicle was hollow, clear and pellucid, and communicated with the ventricular cavity by a small circular orifice. This communication was most distinctly seen on examining the embryo from the dorsal aspect, as shown in fig. 13, where the aperture leading into the protruded sac is visible on one side, bounded by its well-defined margin. In order to satisfy myself of the correctness of this observation, and to test the accuracy of Huschke's statement, I examined numerous embryos every second hour, from the thirty-sixth hour to the time when the above appearances were observed, but in none could I detect a protrusion of the tegumentary layer in that situation, and, coinciding as my observations do with those of Baer as regards the origin of this membrane, they justify, I think, the conclusions which are above stated.

At the fifty-sixth hour (fig. 14) the auditory vesicle occupies its usual position; it has become however increased in size, and has assumed a pyriform shape, so that now it presents a narrow contracted tubular portion, the rudiment of the auditory nerve, and a dilated spherical extremity, the auditory sac, or rudimentary vestibule. This latter portion projects into and becomes encased by the muscular and tegumentary layers of the embryo, forming a distinctly marked projection beneath the integument; the vesicle itself has become darkly granular and more opake, but the cavity in its interior is still distinctly seen communicating with the ventricular cavity, through the tubular prolongation of the vesicle (the auditory nerve); the

aperture of communication is however much smaller, having become more contracted, and this contraction apparently increases as the separation between the auditory vesicle and its parent cell takes place. At the sixty-fifth hour (see fig. 15) the ear-bulb has increased considerably in size, and a more marked separation is now seen to exist between the auditory nerve and the expanded vestibular sac; the latter has assumed an oval shape and is now directed slightly backwards, the cavity in its interior still existing; but the auditory nerve has become now quite solidified, so that no communication exists at this period between it and the ventricular cavity. From the description which I have already given, a marked similarity may be observed between the origin of this membrane and that of the retina and optic nerve; these parts arise in both cases as a protruded portion of the cerebral mass, being hollow and communicating with the cavity of the parent cell; in process of time a gradual separation takes place between them and the parts from which they arise; they then assume a pyriform shape, but still communicate with the cerebral cavity; as however the nerve becomes solidified and more fully formed, and the separation between them is more fully effected, then no communication can be traced between the two cavities. It is in this stage of the development of the auditory apparatus in the Bird, that a remarkable similarity is to be observed between it and the normal condition of the same part in some of the lower animals. There are in fact now formed the two elementary portions of this apparatus, the auditory nerve and its vesicular bulb (the analogue of the vestibular sac). Such is the simple condition of this organ in the crustacea and in the cephalopod mollusks.

I shall, in the next place, proceed to describe the observations I have made on the development of the semicircular canals, or rather of those portions of the membranous labyrinth which line those cavities, and which are found superadded in most Birds, Fishes, and Mammalia.

At the seventy-second hour (fig. 16) the vestibular sac has become more distinctly separated from the cavity from which it originated, but is connected with it by the auditory nerve, which is fully formed and of large size; the vesicle is still quite hollow, and contains a thin limpid fluid; but its oval form is lost from a distinct contraction of its (apparent) entiré circumference, which is observed about its centre; this contraction is seen to exist both on the outer and also on the inner wall, and is the first indication of the separation of the vestibule from the membranous semicircular canals, which are ultimately formed from the terminal portion of the vesicle. At the eighty-second hour (fig. 17) the contraction is observed to have become more marked, so as partially to subdivide the vestibular sac into two unequal portions; the lower one, that connected with the auditory nerve, is the future vestibule, the upper terminal one being developed into the semicircular canals; the cavity still exists in the interior of the vesicle, and the auditory nerve has increased in size. At the close of the fourth day (fig. 18) the terminal bulbous portion of the original vestibular sac has become very considerably enlarged, and of an oval elongated form; the contraction originally

existing and separating it from the vestibule itself has increased very considerably, so that now a well-marked separation is seen to exist, although both cavities communicate with each other. A slight depression or shallow pit is now observed to exist at the end of the terminal vesicle, which soon becomes very distinct. This I believe indicates the first rudiment of one of the semicircular canals; no trace of the folding-in or depression of the integument in this situation could be observed.

About the sixth day this depression is more marked, and it is apparently from the amalgamation of this reflected portion and the inner wall of the vesicle with each other, that the membranous semicircular canals are formed. At first they appear to retain the same diameter throughout, but between the twelfth and thirteenth days they become somewhat contracted in parts, leaving some portions of their original diameter: it is these that apparently ultimately form the ampullæ. At about the same period a cartilaginous nidus is deposited on the outer side of the membranous labyrinth, which is soon developed into the various parts of the osseous labyrinth: at the same time also a small quantity of calcareous matter is deposited in the vestibular sac. It is interesting to observe that the membranous labyrinth between the eighth and thirteenth days has a structure almost precisely similar to that of the retinal expansion of the same period, consisting, like it, of a distinct but very delicate fibrous mesh, in the spaces between which are deposited a quantity of granular matter and numerous nucleated cells, its exterior surface being composed of a dense mass of nuclei, almost precisely analogous to the "agglomerated granules" which form so large a portion of the entire substance of the retina. From the preceding observations the following conclusions may be drawn.

That the membranous labyrinth, like the retina, is a protruded portion of the brain, being hollow and communicating with the ventricular cavity from which it arises. As the progressive development of the brain proceeds, the auditory sac becomes more elongated and of a pyriform shape, the dilated portion being analogous to the vestibule, the contracted tubular portion to the auditory nerve; this subsequently becomes solid, and the cavity in the vestibule does not then communicate with the ventricle, from the wall of which it is an offset. This representative of the normal condition of the organ in some of the lower animals now takes on a higher form of development, for the membranous semicircular canals are now added to the vestibule, being formed by a contraction, and subsequently, a folding inwards and union of a portion of the walls of the vesicle itself; lastly, the walls of these canals becoming in parts contracted, the dilated ampullæ are formed.

Explanation of the Plates.

PLATE VIII.

Fig. 1. An embryo chick at the thirty-first hour of incubation.

Fig. 2. An embryo chick at the thirty-third hour.

Fig. 3. An embryo chick at the thirty-sixth hour. The first rudiment of the eye is here seen to be visible in the form of a protrusion from the anterior cerebral cell.

Fig. 4. An embryo chick at the forty-sixth hour. The optic vesicle is seen now very distinct, presenting a slight contraction at its connection with the cerebral cell from which it arises.

Fig. 5. The cephalic extremity of a chick at the same period more highly magnified. This Plate is intended to represent the cavity which exists both in the cerebral cell and optic vesicle, and the communication between them.

Fig. 6. The cephalic extremity of an embryo at the fifty-fifth hour viewed from the dorsal aspect, principally intended to represent the mode of formation of the crystalline lens.

Fig. 7. The under surface of the eye of a chick at the seventieth hour. This figure shows the spherical form of the eyeball, its contracted tubular end, the optic nerve, the mode of formation of the lens, and the fissure which exists on the under surface of the eye.

PLATE IX.

Fig. 8. The cephalic extremity of an embryo chick at the sixty-second hour (lateral view).

Fig. 9. In this Plate the retina is seen overlapping the margin of the lens at the latter half of the third day.

Figs. 10 and 11. The eye of an embryo chick on the fourth day.

Fig. 12. The eye of an embryo chick on the fifth day.

Fig. 13. In this Plate the first rudiment of the ear is visible in the form of a small vesicular protrusion from the central part of the medulla oblongata (from an embryo chick at the fiftieth hour of incubation).

Fig. 14. An embryo chick at the fifty-sixth hour. The ear-bulb is now seen to be of a pyriform shape, and communicating with the cavity from which it arises.

Fig. 15. The cephalic extremity of an embryo chick at the sixty-fifth hour of incubation. The rudimentary vestibule and auditory nerve are now seen fully formed.

Fig. 16. The ear of an embryo chick at the seventy-second hour of incubation. The

auditory nerve is now seen quite solid, and the vestibule presents a slight contraction near its centre.

Fig. 17. An embryo chick at the eighty-second hour, viewed from the dorsal aspect. The cavity of the fourth ventricle is distinctly seen, and on either side the rudimentary ear is shown *in situ*; the contraction of the wall of the vestibule is more marked.

Fig. 18. The ear of an embryo chick at the ninety-sixth hour. The vestibular contraction is more marked, and a depression is observed at the extremity of the terminal vesicle, which subsequently forms one of the semicircular canals.

8 *Wilton Street*,
October 14*th*, 1849.

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IX. *On the means adopted in the British Colonial Magnetic Observatories for determining the Absolute Values, Secular Change, and Annual Variation of the Magnetic Force.* *By Lieut.-Colonel* EDWARD SABINE, *R.A., For. Sec. R.S.*

Received February 6,—Read April 25, 1850.

So many of the magnetic observatories which professed to adopt and pursue the system of observation recommended by the Royal Society have confined themselves, apparently even in what they have attempted, to investigations into the *diurnal* fluctuations of the magnetic elements, and into what have been called magnetic *disturbances*, that it may not be inappropriate to recall to recollection the far more extensive system of observation which it was the purpose of the Royal Society to institute.

The diurnal variations and the magnetic disturbances form, it is true, a portion, and an important portion, of the objects contemplated; but they can only be regarded as the effects of minor forces, superimposed upon the far more powerful and important agency of the terrestrial magnetism itself, and from which they are probably distinct both in their nature and in their origin.

In the provision of instruments and in the elaborate instructions contained in the Report of the Royal Society for the determination of the *absolute values* and *secular changes*, as well as of the periodical variations of the three magnetic elements, it was obviously the purpose to comprehend as the objects of investigation the *whole* of the phenomena by which the magnetic state of our planet is either permanently or temporarily affected; and particularly the permanent and systematic part of the phenomena which results from that more powerful agency to which the name of "Terrestrial Magnetism" more strictly belongs.

The determination of the mean numerical values of the elements of terrestrial magnetism in direction and force at different points of the earth's surface, (the force being expressed in absolute measure, intelligible consequently to future generations however distant, and conveying to them a knowledge of the present magnetic state of the globe,) and the determination of the nature and amount of the secular changes which the elements are at present undergoing, are the first steps in that great inductive inquiry, by which it may be hoped that the inhabitants of the globe may at some date, perhaps not very distant, obtain a complete knowledge of the laws of the phenomena of terrestrial magnetism, and possibly gain an insight into the physical causes of one of the most remarkable forces by which our planet is affected.

It is true that the instruments proposed by the Royal Society, as well as the in-

structions for their use, were found on the experience of the first few years to be not fully adequate to the satisfactory attainment of all the purposes for which they had been designed. This was especially the case in regard to the Bifilar Magnetometer, the magnet of which, 15 inches long, was directed to be used, in conjunction with the magnet of the Declinometer (which was of similar length), for the determination of the horizontal component of the magnetic force. It was soon found that at a suitable distance from each other, necessarily regulated by their length, the magnets were too far apart in the experiments of deflection, to produce angles of deflection bearing a sufficient proportion to the unavoidable errors of observation; whence the results so obtained were charged with a probable error far too great for the purposes contemplated. It was also found, that, whenever the magnets of the Bifilar and Declinometer were thus employed, a break was unavoidably made in the series with the Bifilar, on the continuity of which its value as a differential instrument, and therefore as an instrument for determining secular changes, must necessarily in great measure depend. To obviate these inconveniences, and particularly the latter, "Revised Instructions" were drawn up and circulated by the Royal Society, recommending the employment of an auxiliary apparatus, by which the experiments of vibration and deflection required for the determination of the horizontal component of the Force might be made in a separate apartment, and therefore without disturbing the magnetometers of the observatory, which from thenceforward would be employed solely as differential instruments. The magnets of the auxiliary apparatus were reduced from 15 inches to 12 and 9 inches in length. It was found however on trial, that when these magnets were placed at the minimum admissible distance from each other corresponding to their length, their distance apart was still too great to produce angles of deflection of sufficient magnitude, to lessen the probable error of the results to an amount, which would enable the secular change from month to month, or even from year to year, to be ascertained by their means within any reasonable period of observation. A few months' additional experience also served to show that when the Bifilar was thus set free to be appropriated wholly as a differential instrument, and when the magnet was left perfectly undisturbed, the conclusions which might be derived from it were still subject to two instrumental irregularities, which did not conveniently admit of elimination by any known process of experiment, and which prevented the observations made with the Bifilar from being strictly comparable with each other for more than very short intervals of time. One of these sources of irregularity had been anticipated, and it was hoped might have been surmounted; but the other had been apparently wholly unforeseen. The first consisted in the liability of the magnet bar to lose a portion of its magnetism. It was hoped if the magnet were entirely undisturbed by removals, that after a few months it might gradually attain a state in which its magnetism might undergo no further change (at least while it remained undisturbed), and that even whilst the period of change continued, the loss might be of a sufficiently uniform character to admit of its being allowed for. This has however

been by no means found to be the case with the magnets employed in the different Bifilars of the Colonial Observatories, whose loss of magnetism appears to be subject to no general or systematic law, and even occasionally to intermit and to recommence without any apparent or discernible cause. To eliminate the effect of the loss, the magnetic moment of the bar would require therefore to be examined from time to time, and at short intervals; but the removal of the magnet for this purpose would break the connexion and thus interrupt the continuity of the series.

The source of the other irregularity in the indications of the Bifilar, and which does not appear to have been anticipated, is still somewhat obscure: the effect is of the opposite character to that of the loss of magnetism in the magnet bar; and the position of equilibrium of the bar has been in more than one instance so much affected by it, that the bar has in a few months progressively passed out of the field of view of the telescope. The position of equilibrium is determined on the one side by the two variables, the magnetism of the earth and that of the bar; and on the other side by the supposed constants, the weight of the bar, the length and distance between the parallel suspension wires, and the angle of torsion. The weight of the bar cannot alter; the angle of torsion and the distance between the wires, observed before and after the change in the instances referred to, were ascertained to have undergone no alteration. A lengthening of the suspension wire has been therefore supposed to be the cause of the irregularity in question, the effect being precisely that which would be produced by an elongation of the wire; but no direct proof of this has yet been obtained, because when the Bifilars were first adjusted no such effect was anticipated, and the exact length of the suspension wire at the period of the first adjustment appears to have been in no case measured*.

The Bifilar being thus found to be affected by two sources of instrumental irregularity opposite in character, neither of which admitted of being satisfactorily eliminated, the comparability of the differential results obtained with that instrument, constructed according to the specifications in the Instructions of the Royal Society, could only be relied on for short intervals, and they would consequently admit of no certain inference being drawn from them in respect to secular changes.

The observations made during the first years of the Colonial Observatories having thus failed in accomplishing a very important, if not the most important, part of the objects contemplated, I requested Captain Riddell, who was at that time my assistant in the superintendence of the British Colonial Magnetic Observatories, to make

* The Toronto Bifilar was adjusted on the 25th February 1843, with the intention that it should remain undisturbed. Between this date and the 11th of October of the same year the reading of the scale had altered 470 scale divisions, equivalent (approximately) to ·044 parts of the force. At Hobarton the Bifilar was adjusted, with the intention of its being left undisturbed, on the 16th of July, 1843. On the 1st of March, 1846, the scale reading had altered 78 scale divisions, equivalent (approximately) to ·017 parts of the force. The alterations in both cases are in the opposite direction to what would be occasioned by a loss of force in the magnet bar, and must be regarded as the excess of one instrumental irregularity over a second, the real value of either being unknown.

such modifications in the Portable Magnetometer originally devised by Professor WILHELM WEBER*, the magnets of which were only from 3 to 4 inches in length, as would be likely to remedy several practical defects which experience had pointed out in that instrument; and to draw up such instructions for its use as might make it, when thus modified, an efficient instrument for effecting those purposes, originally prescribed by the Royal Society, which had hitherto failed of accomplishment; viz. the determination of the absolute values, secular changes, and annual variations of the horizontal component of the magnetic force. The modifications thus introduced and the methods of observation recommended, are contained in a work entitled "MAGNETICAL INSTRUCTIONS *for the use of Portable Instruments adapted for Magnetical Surveys and Portable Observatories, and for the use of a set of small Instruments adapted for a fixed Magnetic Observatory; with Forms for the Registry of Magnetical and Meteorological Observations*;" in which work, various other forms of instruments, suited for particular magnetic purposes, are also described, together with the best methods of using them, and of determining the several constants required in calculating the final results. The Portable Unifilar Magnetometer, with the modifications thus introduced, was shown to the magneticians assembled at the meeting of the British Association at Cambridge in 1845; and Captain RIDDELL's Manual, printed by the authority of Government, has been extensively circulated amongst those persons who are engaged in magnetic researches, and has been found extremely useful, I believe, by those who have consulted it. A statement was made at the meeting of the British Association in 1845 of what had then been accomplished by the Colonial Observatories, and also of what still remained to be accomplished, to fulfil the objects for which the institution of those establishments had been recommended jointly by the Royal Society and British Association; and the probability was shown of speedily fulfilling *all* those objects by the means which had been adopted. Upon this statement a further but limited continuance of the observatories was recommended to Government and sanctioned. I am desirous of taking the earliest opportunity in my power of laying before the Royal Society a statement of the success which has attended the employment of the means thus referred to; because I am in hopes it may be an inducement to other observatories, which have either been instituted for the purpose of cooperating in the plan proposed by the Royal Society, or who have expressed the intention or desire of cooperating, to persevere in the fulfilment of *all* the objects originally contemplated; either by the adoption of the means which will be now described, or by the invention and employment of others which may serve the purpose as well or still more effectually. I shall avail myself of the observations which have been made at the Colonial Observatory of Toronto in Canada, under the direction of Captain

* A description of this instrument, translated by Mrs. SABINE, partly from an original account printed by M. WEBER in the 'Resultate des Magnetischen Vereins,' and partly from manuscript communications kindly furnished by M. WEBER himself, was presented to the Editor of TAYLOR's Scientific Memoirs, and forms art. XVIII. in the second volume of that work.

Lefroy, R.A., F.R.S., for the purpose of illustrating the objects which I have in view. I might also have availed myself of similar observations made at the observatory at Hobarton in Van Diemen Island, under the direction of Commander Kay, R.N., F.R.S., but for the fear of encumbering this communication with too much detail.

The magnets employed for the monthly series of observations on the absolute horizontal force at Toronto are solid cylinders of 0·3 inch diameter; the suspension magnet being 3 inches and the deflecting magnet 3·67 inches in length. The same magnets have been used throughout the series. The observations are made about the same period in every month, and are extended over three days, usually the 16th, 17th and 18th of the month. Three distances are employed, the least being 1 foot, and the greatest 1 foot and four-tenths from the centre of the suspended magnet. The deflections are read on a circle of 6 inches diameter, having two verniers reading to 20″. The deflections vary, according to the distance, from 6° to 10°. The reading telescope is attached to and moves with the azimuth circle; the deflecting magnet is therefore always perpendicular to the suspended magnet when the deflections caused by the latter are read off. The deflecting magnet is suspended for vibration in a stirrup with a mirror, in a detached wooden box, by a silk thread, of which the line of detorsion is brought approximately into the magnetic meridian. The time of vibration is determined by the mean of 300 vibrations in very small arcs, the commencing arc being always the same, *i. e.* 50′, and a correction for the arc is applied. Actual changes in the horizontal force of the earth occurring between the two parts of the experiment, *i. e.* between the experiments of deflection and vibration, are eliminated by a correction derived from the Observatory Bifilar, which is read off concurrently with the deflections and vibrations, and both are reduced by this means to what they would have been, had the horizontal force, at the time of each observation, coincided with the mean horizontal force shown by the Bifilar on the same day. The reduction might obviously have been made with equal convenience to the mean reading of the Bifilar in the *month*; but this reduction would have involved the question of the dependence to be placed on the Bifilar itself for longer periods than for a few hours; and as the absolute determinations extend in every month over three days, I have preferred to keep their results independent of this reduction, except in two instances, viz. October and November 1848, when disturbances of unusual magnitude and continuance lessened the force on the days of observation to a more than ordinary degree. In those two instances therefore the results of the absolute determinations have been reduced to the mean reading of the Bifilar in the respective *months*, instead of its reading on the respective *days* of observation.

Differences of temperature occurring in the experiments of deflection and vibration have been eliminated by a temperature correction applied to the deflecting magnet, in which the coefficient has been very carefully determined by the usual process directed in the Revised Instructions of the Royal Society.

The constant, depending upon the value of the moment of inertia of the deflecting

magnet when suspended for vibration, has been carefully determined by repeated experiments made at Toronto with inertia rings of different weights and dimensions; and for greater security these experiments will be repeated with other rings at Woolwich when the series is closed. The intercomparison of the partial results with all the rings will give to the determination of the value of this constant a probable error, which, converted into terms of the intensity of the force, will enter as one of the constituents into the probable error of the value of the force at Toronto corresponding to the mean period of observation derived from the complete series.

There is also another constant which enters into the absolute value, which has yet to be determined for the Toronto deflecting magnet, namely, that which enables us to eliminate the variation induced by the magnetism of the earth in the magnetic moment of a bar, in the different positions in which it is employed in the experiments of deflection and vibration. An apparatus for the determination of this constant has been constructed at Woolwich, where the necessary experiments will be made at the close of the series; here also a comparison of different trials will give the probable error of the determination of this constant, which will thus enter into and be made a part of the probable error which shall ultimately be assigned to the final mean determination of the absolute horizontal force at Toronto.

For the purposes to be considered in this paper, however, it is not necessary that the values of the constants, representing the moment of inertia and the variation of the induction moment, should be precisely known: the mutual relation of the results obtained in different months would manifestly be the same, although the whole series might be affected by some slight inaccuracy in one or more of the constants employed in the calculation. It is not necessary therefore to wait until the constants above described have been determined with ultimate precision, in order to discuss the probable error of a single monthly determination by the absolute method, and the value of a series of monthly determinations of this nature in investigating the secular change and the annual variation of the force. These will be the same, although the absolute value of the force when finally determined might prove to be one thousandth part greater for example, or one thousandth part less, than we may at present assume it to be.

I subjoin therefore the following series of the results of the monthly observations at Toronto, from January 1845 to April 1849, as *relatively* correct; and as exhibiting the values of the horizontal force on the days of the respective months on which the observations were made, with an accuracy which, as respects observation error strictly so called, must be greater than that which would be inferred from the probable error of a single monthly determination obtained in the usual manner; because the probable error so obtained will include, besides observation error properly so called, the effects of regular or irregular variations which may have affected the force itself on the particular days of observation.

TABLE I.

	1845.	1846.	1847.	1848.	1849.
January	3·5377	3·5378	3·5337	3·5222	3·5213
February	3·5376	3·5313	3·5320	3·5255	3·5210
March	3·5375	3·5341	3·5284	3·5270	3·5240
April	3·5351	3·5323	3·5249	3·5261	3·5260
May	3·5388	3·5317	3·5283	3·5286	
June	3·5421	3·5367	3·5302	3·5274	
July	3·5413	3·5365	3·5287	3·5305	
August	3·5383	3·5313	3·5335	3·5279	
September	3·5373	3·5303	3·5257	3·5239	
October	3·5363	3·5290	3·5251	3·5223	
November	3·5360	3·5278	3·5266	3·5184	
December	3·5379	3·5334	3·5237	3·5214	

Regarding each monthly determination as entitled to equal weight, and taking the arithmetical mean of all the observed values as the most probable mean value, we find the mean value to be 3·53043 with a probable error of ±·00055; and the probable error of a single monthly determination ±·0040.

This is on the most simple hypothesis, in which neither secular change nor annual variation is supposed to exist. If we call X the arithmetical mean as above derived, and X'_1, X'_2, X'_3 ... X'_{59} the several observed monthly results, we shall have the several errors remaining over, X'_1-X, X'_2-X, ... $X'_{59}-X$, as follows:—

TABLE II.

	1845.	1846.	1847.	1848.	1849.
January	+·0073	+·0074	+·0033	−·0082	−·0091
February	+·0072	+·0009	+·0016	−·0049	−·0094
March	+·0071	+·0037	−·0020	−·0034	−·0064
April	+·0047	+·0019	−·0055	−·0043	−·0044
May	+·0084	+·0013	−·0021	−·0018	
June	+·0117	+·0063	−·0002	−·0030	
July	·0109	+·0061	−·0017	+·0001	
August	+·0079	+·0009	+·0031	−·0025	
September	+·0069	−·0001	−·0047	−·0065	
October	+·0059	−·0014	−·0053	−·0081	
November	+·0056	−·0026	−·0038	−·0120	
December	+·0075	+·0030	+·0067	−·0090	

The prevalence of + signs in the earlier portion of the period, and of − signs in the later portion, points obviously to the existence of secular change, viz. to a decrease of the horizontal force in successive years during the period of observation. For the purpose of obtaining the mean annual value of this decrease, we may derive an equation from each of the monthly determinations of the form $X'=X+ay$, in which X is the most probable value of the horizontal force in the middle period of the series, *i. e.* on the 1st of March, 1847, X′ the observed horizontal force in any other month,

a the interval in months between the date of X′ and March the 1st, 1847, and y the monthly variation occasioned by secular change. We have fifty-two such equations furnished by the series, which, treated by the method of least squares, give $X = 3{\cdot}53043$, and $y = -{\cdot}000347$ the monthly secular change, the latter number being equivalent to an annual decrease of ·0042 in the horizontal force during the period comprehended by the observations. For the purpose of obtaining the errors remaining over on this hypothesis of secular change, we must apply to each of the results in Table I. a correction, equivalent to the effect of secular change in the interval elapsed between the dates of the particular observation and the mean epoch of the 1st of March, 1847; and having done so, we now find, on the hypothesis of the existence of a uniform secular decrease of the horizontal force annually of ·0042, 3·53043 as the value of the horizontal force on the 1st of March, 1847, with a probable error of $\pm$·00025; whilst the probable error of a single monthly determination is reduced to $\pm$·0018 instead of $\pm$·0040 as before; and as the weights of different hypotheses are measured by the inverse squares of the probable errors, the hypothesis which supposes a secular decrease of force amounting to ·0042 annually is more probable than the hypothesis which supposes no secular change, in the proportion of 4·7 (nearly) to 1.

Having thus obtained the value of the horizontal component of the magnetic force corresponding to the 1st of March, 1847, and the mean value of the secular change of this element during the period of the observations, we require, for the purpose of deriving the values of the *total* magnetic force and its secular change, at the same epoch, to know the magnetic inclination corresponding to the epoch, and the secular change of that element also. For the first we have to seek the mean result of the observations of inclination, which were also made monthly during the same fifty-two months. In the three first years, 1845 to 1847 inclusive, the observations of inclination were made on every Tuesday and Friday, three hours before noon on the Tuesdays, and three hours after noon on the Fridays; thus furnishing eight or nine partial determinations in each month according to the number of Tuesdays and Fridays contained in it; each determination being complete in respect to the several positions of the circle and needle required for that purpose. In 1848 and 1849 the same number, or occasionally a greater number, of partial determinations was made monthly; but instead of the Tuesdays and Fridays, the days of observation were the same as those on which the horizontal force was observed. The circle employed, from January 1845 to March 1846 inclusive, was one of Gambey's well-known 9-inch circles, and from April 1846 to April 1849 one of Robinson's, of the same dimension and of the same pattern. In Gambey's circle two needles were used, one from January 1845 to December of the same year, and the second from January 1846 to March of the same year; in Robinson's circle also two needles were used, one from April 1846 to August 1847, when an accident befell it, and a second from September 1847 to April 1849. The needles used in Gambey's and Robinson's circles were made by those artists respectively, and both circles and needles were probably as perfect of their kind as any

that have ever been made. The intercomparability of the results might possibly have been more perfect if one and the same instrument had been used throughout (an important consideration in respect to the secular change); but, on the other hand, the probable accuracy of the general result as regards the mean inclination must be viewed as in some degree strengthened by the employment of different instruments. The following Table exhibits the fifty-two monthly results:—

TABLE III.

	1845.	1846.	1847.	1848.	1849.
January	75° 18′·4	75° 13′·8	75° 15′·0	75° 20′·3	75° 19′·5
February	19·5	14·2	15·2	18·7	18·1
March	14·5	13·8	16·2	17·2	16·7
April	11·5	14·3	15·9	18·0	18·4
May	15·4	14·4	16·1	17·2	
June	15·0	14·8	13·1	16·8	
July	14·5	14·0	11·3	16·4	
August	14·6	14·4	12·6	19·0	
September	16·6	15·7	12·5	17·3	
October	14·3	15·4	17·6	19·0	
November	16·8	15·0	17·7	19·4	
December	15·2	15·0	17·0	20·6	

On the hypothesis of the terrestrial magnetic inclination having been constant during the period of observation (*i. e.* constant in respect to secular change and annual variation, and subject only to irregular and diurnal fluctuations), we obtain from the results in the Table a mean inclination of 75° 16′·09, with a probable error of $\pm 0'{\cdot}20$, and $\pm 1'{\cdot}46$ as the probable error of a single monthly determination. These probable errors include of course the effects of irregular fluctuation as well as those of observation error properly so called, besides the possible influence of secular change and annual variation; the two latter being excluded by the hypothesis.

The errors remaining over on this hypothesis are shown in the following Table:—

TABLE IV.

	1845.	1846.	1847.	1848.	1849.
January	+2′·3	−2′·3	−1′·1	+4′·2	+3′·4
February	+3·4	−1·9	−0·9	+2·6	+2·0
March	−1·6	−2·3	+0·1	+1·1	+0·6
April	−4·6	−1·8	−0·2	+1·9	+2·3
May	−0·7	−1·7	0·0	+1·1	
June	1·1	−1·3	−3·0	+0·7	
July	1·6	−2·1	−4·8	+0·3	
August	1·5	−1·7	−3·5	+2·9	
September	+0·5	−0·4	−0·6	+1·2	
October	1·8	−0·7	+1·5	+2·9	
November	+0·7	−1·1	+1·6	+3·3	
December	−0·9	−1·1	+0·9	+4·5	

The prevalence of − signs in the earlier months, and of + signs in the later

months, indicates distinctly the existence of secular change. Pursuing therefore the same method of obtaining its mean value during the period of observation as was adopted in the case of the horizontal force, we obtain from the fifty-two conditional equations $y = +0'{\cdot}0741$ as the monthly value of the secular change, equivalent to a mean annual increase of the inclination during the period of observation of $0'{\cdot}89$; and $75°\ 16'{\cdot}09$ as the mean inclination on the 1st of March, 1847, with a probable error reduced to $\pm 0'{\cdot}17$, the probable error of a single monthly determination being $\pm 1'{\cdot}23$; whence we may infer that the hypothesis of a secular increase in the inclination of $0'{\cdot}89$ annually during the period of observation is more probable than the hypothesis of no secular change, in the proportion of 1·4 to 1.

Total Force; its mean value and secular change.—Having thus derived from the series of fifty-two months of observation the mean value of the horizontal force $= 3{\cdot}53043$, and of the inclination $75°\ 16'{\cdot}09$, each for the epoch of the 1st of March, 1847, we have for the value of the total force in absolute measure at the same epoch $3{\cdot}53043 \times \text{sec. } 75°\ 16'{\cdot}09 = 13{\cdot}8832$. With reference to the inclination element of the result, we might safely regard this value as a final determination; but we cannot quite do as much in respect to the element of the horizontal force, as it may yet have to receive the corrections already noticed (though they are likely to be extremely small), when the values of the constants of inertia and induction shall be finally ascertained on the return of the instruments to Woolwich. When these constants and their probable errors are known, the probable error of the finally corrected value of the total force will also be assignable.

The elements from which we have to infer the *secular change* of the total force are the secular changes of the horizontal force and of the inclination derived from the observations; these are an annual decrease of ·0042 in absolute measure of the horizontal force, and an annual increase of $0'{\cdot}89$ of inclination. A secular change of the horizontal force may be produced, either by a secular change of the inclination affecting the horizontal component of the total force according to the known principles of the resolution of forces, or by a secular change in the total force itself; or, finally, it may be the joint production of both. An increase of the inclination causes a decrease of horizontal force, and *vice versâ*; so far therefore we may regard the annual decrease of the horizontal force at Toronto as attributable in part at least to the annual increase of the inclination. But an annual increase of $0'{\cdot}89$ in the latter element is equivalent to an annual decrease in the horizontal component of the force of not more than ·0035. There remains, therefore, an excess of ·0007 in the secular decrease of the horizontal force, which is unaccounted for by the secular change of the inclination, and is indicative of the existence of a small annual decrease in the total force during the period of observation. The uncompensated portion of the horizontal force on which this inference is founded is indeed small in absolute amount, but its magnitude must be judged of in relation to the probable errors

of the determinations of secular change of the inclination and horizontal force. Viewed in this light, the probabilities are in favour of the existence of a small annual decrease in the total force, as the legitimate conclusion from the portion of the series of absolute determinations in progress at Toronto which has been received in this country, and is here discussed: whilst it is obvious that the groundwork is laid of a positive conclusion, admitting of no uncertainty, attainable by steady perseverance in the prolongation of the series; avoiding as far as possible, upon all occasions, all changes in the instruments employed or in the methods of observation. It will be shown in the sequel that certainty in respect to the question, whether the total force at Toronto is at the present epoch increasing or decreasing, may have a very considerable theoretical importance.

Annual Variation.—We may now proceed to a consideration of the inferences which the observations will afford in regard to annual variation; but in entering on this investigation, we must remember, in the first place, that fifty-two months constitute but a short period from which to derive an *annual* variation; and in the second place, that we are as yet unable to eliminate the effects of the *irregular* disturbances from the residual errors, which consequently remain charged with them to the last; and that if these effects are not themselves the sole cause of an annual variation, by reason of their greater frequency or magnitude at certain seasons of the year than at others, we must be prepared to expect that they will embarrass the research, by rendering the effects of other causes less apparently systematic than they would otherwise have been found. In the horizontal force particularly we may have reason to apprehend the influence of disturbances, because that element is greatly affected by them at Toronto, and their average effect appears to be to depress the force at the periods of their occurrence below its mean value.

We have shown in the preceding pages the fifty-two monthly results of the observations of the inclination and horizontal force, and their arithmetical means constituting the mean values of those elements on the 1st of March, 1847; we have also derived from the observations the most probable values of the secular change of the elements during the period of observation. When each of the fifty-two results has received a correction for secular change proportioned to the interval of time elapsed between the date to which it refers and the 1st of March, 1847, and the differences are taken between the fifty-two results thus corrected and the arithmetical means, we obtain a suite of residual quantities, by which the influence of annual variation, if it exists, might be expected to be indicated. The following Table exhibits the mean difference in each month of the observed results, (when corrected as above noticed for secular change,) from the arithmetical means.

TABLE V.

	Residual quantities.	
	Inclination.	Horizontal force.
	′	
January, mean of 5 years	+1·40	−·0004
February, mean of 5 years	+1·06	−·0012
March, mean of 5 years	−0·44	·0000
April, mean of 5 years	−0·58	−·0010
May, mean of 4 years	−0·38	+·0002
June, mean of 4 years	−1·03	+·0028
July, mean of 4 years	−1·93	+·0033
August, mean of 4 years	−0·90	+·0022
September, mean of 4 years	+0·13	−·0009
October, mean of 4 years	+0·35	−·0017
November, mean of 4 years	+0·97	−·0023
December, mean of 4 years	+0·60	−·0002

When due allowance has been made for the shortness of the period of observation, and for the influence of disturbing action, we find in this tabular view a much more conclusive indication of the existence of annual variation than we might perhaps have been prepared to expect. The inclination is obviously highest in the winter months and lowest in the summer months, passing through its mean value about the period of the equinoxes. The horizontal force has a corresponding variation, but with opposite signs. The occasional irregularities are more marked in the horizontal force than in the inclination, and in both they prevail chiefly in the months of spring and autumn. It must remain for a separate discussion, to deduce from the great mass of facts which have now been collected at Toronto, the numerical conclusions which they will afford in regard to the frequency and magnitude of the disturbances in the different months of the year; but antecedently to the certain conclusions to be drawn from such numerical values, it is not an improbable supposition, that the months of spring and autumn (and notably those of autumn) may prove to be generally the most disturbed months, and consequently those of the greatest depression of the horizontal force resulting from the disturbances. The irregularities may be expected to diminish as the series is extended; but if they are, in part at least, occasioned by actual irregularities in the force itself produced by the disturbances, they may have a character of permanency in certain months which no continuation of the series would remove, if it should prove that the disturbances prevail more in some months than in others, and if their action has on the average a special tendency.

In commenting on the fortnightly means of the Bifilar observations at Toronto in 1842*, (in which year the Bifilar observations were suitable for the investigation, inasmuch as the scale-reading returned nearly to the same division at the close, as that at which it had stood at the commencement, of the year,) I called attention to the remarkable feature, indicated by the Bifilar readings, of an excess in the value of the horizontal force in the summer months over the other months of the year; and I

* Toronto Observations, vol. i. p. xxxvii and xxxviii.

remarked on that occasion, that "the excess appeared to be too large to be caused by any conceivable error in the determination of the temperature correction of the magnet, or generally of the apparatus by which it was suspended." The average difference between the summer and winter months, derived from the observations of the Bifilar in the single year referred to, was ·00161 parts of the whole horizontal force, or ·0056 in absolute measure.

The question of an annual variation of the horizontal force appeared to me so important either to verify or disprove, that, at my request, Captain Lefroy employed, during the years 1847 and 1848, a third method of experimenting, which, although it may not be quite so satisfactory in respect to the individual monthly results as the method of absolute determinations, in consequence of the magnetic moment of the bar not being subject to monthly examination, has yet the advantage of affording a third conclusion perfectly independent of the others, and but little inferior to the absolute method in proportion to the time of their respective continuance. One of the cylindrical magnets of 3·67 inches in length, which had been employed in the North American survey, and appeared to have attained a state of steady magnetism (which however did not prove so thoroughly steady as was expected), was suspended in the usual manner in a light stirrup, with an attached mirror and a detached telescope. The horizontal force of the earth was measured at stated hours, twice in every day, at 10 A.M. and 5 P.M., by the times of vibration of the bar derived from four hundred vibrations observed in the usual manner, and reduced to a standard temperature and to infinitely small arcs. The magnetic moment of the bar was carefully examined before the commencement and after the conclusion of the series, viz. on the 31st of December, 1846, and on the 3rd of January, 1849, and also intermediately on January 5th, 1848. The magnetic moment at these periods was as follows:—

		Loss of magnetism in nearly equal intervals.
1846. December 31st	=0·6104	·0104
1848. January 5th	=0·6000	·0087
1849. January 3rd	=0·5913	

The value of the magnetic moment has been assumed on the hypothesis of uniform loss of magnetism in the whole period, and has been computed for every day of observation. Now if we take the arithmetical mean of the absolute values of the force in the twenty-four months derived by this bar as the mean result corresponding to the 1st January 1848, and if for the purpose of eliminating secular change we combine the values in January 1847 and December 1848, February 1847 and November 1848, &c., we obtain the excess or defect in the horizontal force in absolute measure for the months of winter and summer as follows:—

TABLE VI.

Winter	January	1847 and December	1848	−·0043	−·0038
	December	1847 and January	1848	−·0034	
	February	1847 and November	1848	−·0039	
	November	1847 and February	1848	−·0037	
Summer	May	1847 and August	1848	−·0006	+·0047
	August	1847 and May	1848	+·0042	
	June	1847 and July	1848	+·0084	
	July	1847 and June	1848	+·0070	

We have here a still further confirmation of the greater amount of the horizontal force in the summer than in the winter months; the difference between the two seasons is in this experiment greater than that shown by the Bifilar observations for 1842, or than that derived from the more extended absolute series from January 1845 to April 1849. It is quite conceivable however that, independently of errors of measurement, the actual numerical difference between the summer and winter months may be liable to vary in different years.

By three independent methods of experiment, therefore, the general fact of an annual variation of the horizontal force at Toronto has been shown, the force being greater in the summer than in the winter months; but the question of whether this variation, as well as that of the inclination, is progressive from one extreme in midwinter to the opposite extreme in midsummer, and *vice versâ*, the regularity of the progression being only interrupted by the complication of irregular disturbances,—or whether, as in the case of the diurnal variation, the change from one half-yearly phase to the other takes place (subject to the same complication) about the time of the equinoxes,—will require a longer period for its determination than that which we have at present before us. Upon the latter supposition, we find, from the absolute series at Toronto, that the inclination is on the average 0′·88 above its mean value, and the horizontal force ·0015 below its mean value during the five months when the sun is in the southern signs,—and the inclination 0′·90 below, and the horizontal force ·0011 above, their respective mean values, when the sun is in the northern signs.

The sum of the differences of the inclination at the opposite seasons (1′·78) is equivalent, in the resolution of the total force into its horizontal and vertical components, to ·0070 of horizontal force. The annual variation of the horizontal force derived from the observations, corresponds in *direction* in each of the seasons to that which is indicated for it by the change of the inclination, but the *amount* falls considerably short of that which would be the equivalent of the alteration in the latter element. Hence we must infer the probable existence of an annual variation of the total force, the force being greatest in the winter months, or when the sun is in the southern signs; and least in the summer months, or when the sun is in the northern signs.

Although I have been unwilling to encumber this communication with details from the Hobarton Observatory similar to those from Toronto, I may be permitted to state very briefly the *results* obtained at Hobarton in respect to the annual variation of the Inclination and Force, as they have a very considerable interest when viewed in connection with those obtained at Toronto.

A series of monthly determinations of the inclination, in which no change was made in the instruments employed, or in the methods or place of observation, was commenced at Hobarton in June 1843, and was still continuing at the date of the last returns received from thence in December 1848. From this series we have sixty-eight consecutive monthly determinations, strictly intercomparable, bearing on the question of annual variation. It will be remembered that the summer of the southern hemisphere is when the sun is in the *southern* signs, and *vice versâ*; and that at Hobarton it is the *south* end of the needle which dips below the horizon. The investigation, conducted in the same manner as at Toronto, shows at Hobarton a decrease of *south* inclination of 0'·89 on the average of the months from April to August inclusive, *i. e.* in the southern winter; and an increase of 0'·85 from October to February inclusive, *i. e.* in the southern summer. Thus in the months from April to August the North Inclination at Toronto and the South Inclination at Hobarton are both diminished; and from October to February inclusive they are both increased. The North Inclination at Toronto is lowest and the South Inclination at Hobarton highest, in the respective summers of the two stations, and *vice versâ*, and in both cases the variation is nearly to the same amount.

In the case of the horizontal force, a regular and consecutive series of monthly determinations, similar to that at Toronto, was commenced at Hobarton in January 1846, and the results have been received in England to December 1848 inclusive. The series treated in a similar manner to that at Toronto shows an annual variation of the same character as respects the seasons, and almost identical in amount with that at Toronto. In the months from October to February inclusive (or in the summer months at Hobarton), the horizontal force is ·0017 *greater* on the average than its mean amount, and from April to August inclusive (or in the winter months at Hobarton), it is on the average ·0013 *less* than its mean amount.

The inferences to be drawn from these variations of the inclination and horizontal force taken conjointly, as respects the total force at Hobarton, are as follows: the inclination being greater from October to February than from April to August, if the total force remained unaltered, the horizontal force should be *below* its mean amount in the months from October to February, whereas we find a *higher* amount in those months; therefore, so far as the observations have yet gone, the total force at Hobarton appears to be subject to an annual variation, being *higher* than its mean amount from October to February, and *lower* than its mean amount from April to August.

It may assist the recollection of the facts regarding the annual variation of the two

magnetic elements at Toronto and Hobarton to state;—that in the months from October to February the magnetic needle more nearly approaches the *vertical* direction at both stations, and from April to August the *horizontal* direction;—and that the total force is greatest at both stations from October to February, and least from April to August.

It is much to be desired that so remarkable a result should receive a full confirmation, by the continuance of the observations at Toronto and at Hobarton for such an additional period as may appear necessary for that purpose; and that the general conclusion indicated by the observations at those stations should be verified by similar investigations in other parts of the globe, especially at the observatories which now exist. The facts, as far as they go, indicate the existence of a general affection of the whole globe having an annual period, and would appear to conduct us naturally to the position of the earth in its orbit as the first step towards an explanation of the periodic change*. It might possibly be regarded as premature, in the present stage of the inquiry, to enter on the discussion of such physical hypotheses as may present themselves on the supposition of a causal connection of this nature; but it cannot be open to the same objection, to press on the consideration of those who are engaged in experimental researches in terrestrial magnetism, (or of others who may have it in their power, from station or influence, to give countenance or support to those who are so engaged), the importance of following up without delay, and in the most effective manner, a branch of the research which gives so fair a promise of establishing a conclusion of so much theoretical moment upon the basis of competent experiment†.

I may be permitted, in conclusion, to advert, though very briefly, to considerations which may give a particular importance to accurate numerical values of the magnetic elements and their secular changes determined at Toronto.

That station was selected on account of its proximity to one of those remarkable points on the globe which have a peculiar importance in theoretical respects: viz. to one of the two points in the northern hemisphere which are the centres of the loops

* The portion of the year when the magnetic force is greatest and the direction of the needle most vertical in both hemispheres, viz. from October to February, coincides with that in which the earth is nearest to the sun, and also moves with greatest velocity in her orbit. There is another curious annual coincidence of a wholly different nature, unconnected with the position of the earth in her orbit; during the months from October to February, when the magnetic force is greatest and the direction of the needle in both hemispheres most vertical, Mr. Dove's recent investigations have shown that, owing to meteorological causes traceable to the unequal distribution of land and sea in the two hemispheres, the aggregate temperature of the whole earth is lower than in the opposite period of the year.

† I am glad to be able to add, that by a letter received from Lieut. Gilliss of the United States Navy, Director of the Astronomical Observatory established at Santiago in Chili, magnetical observations, similar to those referred to in this communication as being in progress at Toronto and Hobarton, were commenced at Santiago in January of the present year, with instruments which had been prepared at Woolwich at the expense and by the request of the Government of the United States.

of the isodynamic lemniscates (as they have been usually called), and are the points of greatest intensity of the force (on the surface of the globe) of apparently two magnetic systems, distinguished from each other by the very remarkable difference in the rate of secular change to which the phenomena in each system appear to be subject. In the present state of the terrestrial magnetic phenomena, the principal of these two points, or the centre of the larger loop of the lemniscates, is situated within the British territories in North America; and by the magnetic survey of those territories, undertaken by the British Government on the recommendation of the Royal Society, and executed in 1842 and 1843 by Captain Lefroy, its geographical position was approximately ascertained, and the difference between the magnetic force at this central point and at the Toronto Observatory was very carefully measured, and is recorded in the Philosophical Transactions (Part III. for 1846). In this point of view therefore the accurate determination of the Force at the observatory at Toronto has a peculiar value, both for the present and for after times. It will, I think, be clear to those who have followed the details of this communication, that by the skill, assiduity and perseverance of the Director of the Toronto Observatory and his assistants, (non-commissioned officers of the Royal Artillery,) this object has been accomplished within very small limits of uncertainty as dependent on observation or accidental error; and that when the small corrections which have been noticed, as requiring to be investigated on the return of the instruments to England at the close of the series, have been ascertained and applied, the value of the total force in absolute measure at Toronto, and by its means the value at the central point, will be assigned with a degree of accuracy which we may believe will be regarded as satisfactory, not only at the present day, but at those distant periods, when the determination may be referred to as presenting the earliest record of the value of the terrestrial magnetic force at its point of maximum in the northern hemisphere.

The determination of this value at this particular time may derive an additional importance from the present relative situation of the two magnetic centres* which are not yet far removed from their greatest distance apart, viz. 180° in geographical longitude; a state of the phenomena constituting possibly an epoch in the cycle of secular change, characterized by that portion of the force at each centre which is derived from mutual influence being a minimum. The analogy of the southern hemisphere, where the two centres are nearer to each other in respect to geographical longitude than in the northern hemisphere, and where the force at each is higher than at the corresponding northern centre, may justify this supposition. The geographical longitude of the principal northern maximum was ascertained by Captain Lefroy, in the years 1842 and 1843, to be about 270° East; that of the minor maxi-

* It will of course be understood that by the employment of the word "centres" it is not intended to convey that the points of maximum are themselves centres of the magnetic force of the systems to which they may respectively belong. The expression is merely used to designate central points of certain phenomena observed on the earth's surface, where alone it is in our power to observe them.

mum, in the same hemisphere, was determined a few years earlier (1828 and 1829), by the expedition of MM. Hansteen, Erman and Due; and we may gather the result from the following passage in M. Erman's 'Reise um die Erde,' which I quote from Mr. Cooley's translation, vol. ii. p. 365:—"The magnetical results of the last journey were now examined more narrowly, and it was clear that we had in fact crossed the meridian of the Siberian magnetic pole between Irkutsk and Yakutsk. The magnetic attraction of the earth was decidedly greater between Kirensk and Beresovoi Ostrov than at any other point which we had visited in the same parallel of latitude to the east or west. The pole sought for had there exhibited its greatest force, and extended its influence furthest to the south; and consequently we must have been there on the same meridian with it. This probably took place at Parshinsk in longitude 111° 27′ E.*." Omitting the consideration of the small amount of secular change which may have taken place between the expedition of MM. Hansteen, Erman and Due and that of Captain Lefroy, we have here an interval of (270° −111°=)159° as the approximate difference of longitude (on the side of Behring's Straits and the adjacent continents) between the two northern centres. This difference is diminishing by the effect of secular change, and the epoch, when the centres were 180° apart, must therefore have taken place a few years antecedently to either of the determinations above referred to; probably about the close of the last century, when, as we learn by Professor Loomis's discussion of the observations of magnetic inclination in the northern parts of the United States†, the inclination which had previously diminished in that quarter began to increase.

The change in the geographical position of both the points of maximum in the northern hemisphere has been from west to east since the earliest period at which inferences of this nature could be drawn from the phenomena; the diminution of the meridional distance between them on the one side, and its increase on the other, being occasioned by the more rapid movement of translation of the minor maximum. It has been conjectured that the motion of the principal maximum might cease to be progressive in the easterly direction when the two centres or maxima should be 180°

* It is obvious that M. Erman uses the term "magnetic pole" to designate the central point of a loop of the isodynamic lemniscates, or the point of greatest intensity of the force. This also is the sense in which it is employed by M. Kupffer, when he says "il y a un pole magnétique dans la Sibérie." The term "pole" cannot however be understood to have the same signification in those writings which assert a supposed connection between "two magnetic poles" and "two poles of cold" in the northern hemisphere; for, in North America at least, the point of maximum intensity of the force is certainly very far distant from that of the lowest annual temperature: the "magnetic poles" in this case may possibly be intended to refer to the centres of the loops of the *isoclinal* instead of those of the *isodynamic* (so-called) lemniscates. But either of these significations differs materially from M. Gauss's definition of a magnetic pole, *i. e.* "where the horizontal terrestrial force is zero." I have subjoined this note in illustration of some remarks which I ventured to make in a former communication on the inconvenience of the employment of a term which appears to be used in different meanings by different writers.

† In Silliman's Journal.

of geographical longitude apart, and that it might thenceforward be retrograde. The observatory at Toronto seems well situated for deciding this question. If the progression of the secular change of both systems continues to be the same after that epoch is past as it was before, the force at Toronto might be expected to sustain on the whole an annual *decrease*, as it would be more diminished by the recession of the neighbouring greater maximum, than increased by the approach of the far more distant minor maximum. If, on the other hand, the movement of the principal maximum should be retrograde, the force at Toronto might be expected to undergo a considerable annual *increase*. By the observations which have been discussed in this paper, it has been shown that the probabilities are considerably in favour of the existence of a small annual *decrease* of force at the present time: and as time alone is wanting to convert this probability into certainty, it would seem particularly desirable that the series of monthly observations of the horizontal force and of the inclination at Toronto should be continued, until the direction and approximate value of the secular change of the total force shall be thoroughly determined.

X. *Observations on the Freezing of the Albumen of Eggs.* By James Paget, *Esq., Professor of Anatomy and Surgery to the Royal College of Surgeons of England. Communicated by* Thomas Bell, *Sec. R.S.*

Received September 26, 1849,—Read January 24th, 1850.

In 1777, John Hunter communicated to the Royal Society a series of experiments on the heat of animals and vegetables, among which were some showing that an egg, after having been frozen and thawed, will, on a second exposure to cold, freeze more quickly than it did before, and more quickly than a fresh egg does when exposed to the same temperature. From these and other experiments, he concluded "that a fresh egg has the power of resisting heat, cold and putrefaction in a degree equal to many of the more imperfect animals;" and he adds, "it is more than probable this power arises from the same principle [*i. e.* a living principle] in both*." Mr. Hunter's pupils generally adopted this conclusion: and the facts on which it was based have formed a chief part of the evidence for the existence of a special vital principle capable of resisting, by a kind of passive opposition, the changes that physical forces produce in dead organic matter.

In the course of some inquiries into the nature of the life of the blood, I repeated and extended Mr. Hunter's experiments, and obtained results which, I venture to hope, may be deemed worthy of the consideration of the Society.

My experiments consisted chiefly in submitting to temperatures near to zero of Fahrenheit, fowls' eggs, into which thermometers with slender bulbs were introduced. The decrements of heat were registered every minute, and the time was noted at which each egg began to freeze, the general indication of that event being the swelling of the albumen, and its protrusion from the aperture through which the thermometer was passed.

I found, as Mr. Hunter did, that a fresh egg generally resists freezing longer than one does which, having been previously frozen and thawed, is exposed, in all similar circumstances, to the same temperature. The result of twenty experiments, in which such eggs were placed in temperatures ranging from zero to 10° Fahr., was, that the fresh eggs were frozen, on an average, in 26 minutes, and the eggs that had been previously frozen and thawed, were frozen for the second or third time in 15¼ minutes.

I next determined, by similar experiments, the respective times of freezing of fresh eggs, and of such as were variously changed in structure and chemical composition. Similar results appeared. If the yelks of the eggs were broken, so as to be mingled

* Hunter's Works, by Palmer, vol. iv. p. 150.

with the albumen; if their whole substance were decomposed, so as to emit a more or less putrid odour; if a powerful electric shock had been passed through them,—in all these conditions, they froze more quickly than fresh and uninjured eggs did, that were exposed with them to the same low temperature. The average difference in the respective times of freezing was nearly the same as that already stated.

All these experiments tended to confirm Mr. Hunter's explanation; for all seemed to show that, by the influence of such forces as commonly destroy animal life, eggs lose some capacity of resisting the abstraction of heat. But when I examined the registers of the decrements of heat sustained by the several eggs during each minute of their exposure to the cold, it appeared that the fresh eggs almost always lost heat more rapidly than those did which had been frozen, broken, decomposed, or electrified. An average result of experiments upon thirty-three eggs of each class was, that, between the fifth and fifteenth minutes after first exposure to a temperature of from 5° Fahr. to 10° Fahr., the fresh eggs lost 17° of heat, and the others only 13¾°. The reason why the fresh eggs, though they lost heat more rapidly than the others, yet were longer in freezing, was, that in most cases their temperature was reduced some degrees below 32° before freezing took place; while the eggs that had been frozen before, or that were in any other way spoiled, always began to freeze as soon as they reached the temperature of 32°.

Mr. Hunter had remarked this difference. In one of his experiments, he says, "a fresh egg sank to 29½°, and in twenty-five minutes later than the dead one, it rose to 32°, and began to swell and freeze." But I found that fresh eggs could be reduced to a much lower temperature without freezing. In several experiments they fell to 20°; in some to 16°, before, with a rapid rise to 32°, freezing took place; and from some observations, which will be hereafter mentioned, I believe that, under favourable circumstances*, the temperature of a fresh and unbroken egg may be reduced to within 5° of zero of Fahrenheit without freezing, although its proper freezing-point, and that to which its temperature rises when it begins to freeze, is 32° or between 31° and 32°†.

It thus appeared that a fresh egg does not resist freezing as a living animal does, which either parts with its heat slowly, or else produces heat, compensating in some measure for that which is lost. It is as much the peculiarity of the fresh egg to lose its heat more quickly than another does, as it is to be longer in freezing; and, indeed, this quicker loss of heat seems essentially connected with the ability to be reduced far below 32° without freezing; for, among thirty-two fresh eggs, there were eleven which began to freeze at 32°, and all these had lost heat slowly; the average decrement between the fifth and fifteenth minutes of their exposure to cold being only 13¾°.

* The chief of these circumstances are, that the egg should be unmoved, and that its albumen should be not even so much disturbed as it is by the introduction of the thermometer.

† With so slender thermometers as I was obliged to use, it was not possible to determine within half a degree the precise freezing-point.

Many things observed in the course of these experiments seemed to indicate that the freezing of the fresh egg was retarded by some peculiarity of its mechanical construction, which was destroyed by the several means supposed to destroy its life. It was, therefore, desirable to ascertain whether the capability of being reduced far below 32° without freezing, and the consequent apparent resistance to freezing, could be destroyed by any means that would not at the same time prevent the egg from manifesting, by development in incubation, the surest evidences of vitality. In experiments to determine this point, I found that one might, with a bent probe, gently detach the whole of the albumen of an egg from its connection with the membrane of the shell, and that after this the chick would be developed, although, perhaps, not to perfection. But when eggs with the albumen thus disturbed were exposed to cold, they did not descend below 32° without freezing; they lost heat less quickly, but froze sooner, than uninjured eggs did, when exposed with them to the same temperature; they froze like the eggs which Mr. HUNTER considered dead.

Again, cracking the shell of an egg does not prevent the development of the young bird, although, in consequence of the excessive evaporation through the fissures, the development may be imperfect. But when eggs with their shells cracked in many places, and with slight injuries of the membrane of the shell, were exposed to cold, they lost heat and froze just as those did which might be reputed dead. Thus, then, mechanical injuries, such as could not have affected the chemical composition of the fresh egg, and such as did not prevent its development in incubation, were found sufficient to deprive it of its power of resisting freezing; and thus its power of resistance appeared to be due, not to any vital principle, but to some peculiarity of mechanical construction.

It may be very difficult to prove what this peculiarity of construction is. That it is a property of the albumen was proved by some experiments, in which albumen, gently removed from fresh eggs, exhibited the same mode of freezing as the entire fresh eggs did: and the following facts, as well as those already mentioned, are favourable to the opinion, that the property which enables fresh albumen to descend far below 32° without freezing, is its peculiar tenacity or viscidity, by means of which the water combined with it is held so steadily, that the agitation favourable, or even necessary, to the freezing at or near 32° cannot take place.

1. The decay and putrefaction of an egg, the freezing and again thawing of one, and (as egg-preservers well know) the stirring and frequent concussion all tend to diminish the viscidity of the albumen to such a degree, that, instead of forming a consistent substance, the greater part of it will flow like a thin liquid from an aperture in the egg-shell.

2. The albumen of eggs does not freeze like a dense solution of albumen, or of saline substances, in water, but like water of which the ordinary freezing is prevented. The freezing-points of aqueous solutions are, according to their densities, more or less below 32°; and if, in exposure to intense cold, the temperature of any

such solution be reduced below its freezing-point, it will, at the instant of freezing, rise to that point, whatever it may be, and not to 32°. Thus, I placed in a freezing-mixture of which the average temperature was 10° Fahr., solutions of common salt in the proportions of 3, 5, 6 and 9 parts to 100 of distilled water; they fell to from one to six degrees below their several freezing-points, and then, in the act of freezing, rose respectively to 28°, 25°, 24½°, and 23°. At these temperatures they remained till they were thoroughly frozen, and then they all descended to the temperature of the medium in which they were placed. The same is observable in the freezing of serum and blood, which, in their relations to heat, may be regarded as mere solutions of albumen and saline matters: they freeze at from 29° to 31°, and retain these temperatures till they are thoroughly frozen. I found the same also in the freezing of milk and of thick mucilage of gum; the former froze at 30°, the latter at 28°, but neither of them in freezing rose to 32°. Unlike all these substances, the albumen of fresh eggs, however far below its freezing-point it may have descended, always in freezing rises to 32°; it freezes therefore like water, or like a very weak saline solution, which, by some mechanical disposition of its particles, is prevented from freezing as soon as it is reduced to 32°, or a few degrees lower.

3. The sudden strong agitation of fresh albumen, when its temperature is reduced several degrees below 32°, will often cause it to freeze at once*, as water under the same circumstances freezes.

4. It is well known, that when once a portion of any given quantity of water is frozen, the portion in contact with the ice cannot be reduced below 32° without freezing. I thought, therefore, that if I could bring ice just formed into contact with the albumen of an egg, the water in the albumen would freeze as soon as it fell to 32°, and so it proved; for in three experiments, in which the air-cavities of fresh eggs were filled with water before exposing them to cold, the albumen did not descend below 32°, but froze at that temperature.

Whether the explanation here offered of the peculiar property of the albumen of fresh eggs be right or not, the property will, I think, merit consideration in reference to both the nature and the purpose of the substance to which it belongs.

For, in regard to the nature of this form of albumen, its mode of freezing proves it to be essentially different both from all solutions of albumen and from organic tissues holding albuminous matter in suspension. As I have already stated, the freezing-

* In the course of the experiments, I observed that the effect of agitation, on either albumen or a saline solution, when its temperature is reduced below its freezing-point, depends in some measure on the temperature of the medium in which it is placed. Thus a saline solution, whose freezing-point was 28°, might be reduced to 25° in a medium of 24°, and, on being now agitated, it would not freeze; but a similar solution, reduced to 25° in a medium of 10°, would freeze at the instant of agitation. In a medium of which the temperature averaged 21°, no length of exposure and no agitation would, in one of my experiments, make albumen freeze, though it fell to the temperature of the medium; but in others, when albumen, in a medium averaging 10°, fell to 28°, it froze as soon as it was agitated.

points of albuminous solutions are lower than 32° in direct proportion to their densities; they do not, in freezing, rise to 32°, but freeze in all respects like saline solutions. And the same mode of freezing may be observed in organic tissues in which albuminous fluids are suspended or infiltrated. An eye, or its vitreous humour, a piece of muscle, gland, or brain, exposed to intense cold, loses temperature to 32° or 31½°, and remains at this, its freezing-point, till it is frozen hard throughout, and then descends to the temperature of the medium in which it is placed.

The purpose or utility of this peculiar property of the albumen of eggs is manifest in the defence which it provides for eggs exposed to a temperature below 32°. If an egg be frozen, the damage sustained by its structure is such that the germ cannot be fully developed; but mere cold, however intense, if freezing does not take place, does not prevent the complete development of the young bird. I placed three eggs in a freezing mixture, varying from zero to 5° Fahr.: one of them froze, and its shell was cracked from end to end; another froze, and when it thawed, its yelk was burst and mixed with the albumen. In incubation, two spots of blood were developed in the former, and an enlargement of the cicatricula ensued in the latter of these two eggs,—sufficient indications that the intense cold and freezing had not killed them, though it had spoiled their structure. But in the third egg, which had been exposed for nearly an hour to a temperature below 5° Fahr., perfect development took place in incubation. Even this degree of cold therefore had neither killed nor frozen the egg, though, according to the average rate at which eggs part with heat, its whole substance must have been for half an hour at a temperature between 5° and 10° Fahr.

This security of eggs from the injurious influence of cold has also been proved, on a large scale, by the ingenious inventor of the hydro-incubator, Mr. Cantelo. He has told me, that, to test the truth of the popular belief that eggs are always destroyed by exposure to a frosty air, he sometimes exposed baskets of eggs, through the whole of a Canadian winter's night, to a temperature ranging, he believes, between 5° and 10° Fahr. Some of them were cracked, and these he threw away; they were doubtless frozen and spoiled; but the rest were placed in his incubator, and the usual proportion were hatched.

The need of such a provision against the influence of cold must exist in the case of many, or perhaps of all, birds that breed in cold climates; for accident must occasionally drive from their nests even those parent-birds that have not, like the common fowl, the custom of leaving their eggs for a certain time exposed to the open air.

In conclusion, I may repeat that the experiments I have related show that it is not by the power of a vital principle that eggs resist the influence of cold. They show that certain things will destroy the power of resisting cold without affecting the capability of being developed, and of therein manifesting the best evidence of life; and that when eggs yield to the influence of intense cold, they are not damaged unless

they are frozen, and are not killed even when frozen. The experiments thus remove almost the only remaining support of the hypothesis that such a vital principle may exist in organized bodies, as may enable them, even while inactive and displaying no other signs of life, to resist passively the influence of physical forces.

XI. *Researches on the Tides.—Fourteenth Series.*

On the Results of continued Tide Observations at several places on the British Coasts.

By the Rev. W. Whewell, *D.D., F.R.S.*

Received October 24, 1849,—Read January 31, 1850.

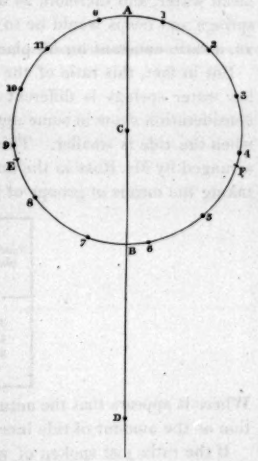
TIDE observations made at several different parts of the British and the neighbouring shores, and in some instances continued for a considerable period, have been discussed by Mr. D. Ross of the Hydrographer's Office, with great labour and perseverance; and as the results which his labours afford may be of use to mariners, I offer to the Royal Society a brief statement of these results.

The discussions at present referred to relate to the height of high water, and the variations which this height undergoes in proceeding from springs to neaps and from neaps to springs. It is found, by examining the observations at 120 places and throwing the heights into curves, that the curve is very nearly of the same form at all these places. Hence the semimensual series of heights at any place affords a rule for the series of heights at all other places where the difference of spring height and neap height is the same. For instance, Portsmouth, where the difference of spring height and neap height is 2 feet 8 inches, is a rule for Cork, Waterford, Inverness, Bantry, Boucout on the French coast, and other places.

And the Tables of the height of high water at one of these places suffice for all the others, a constant being of course added or subtracted according to the position of the zero-point from which the heights at each place are measured.

The series of heights of high water for a semilunation also agrees very exactly, as to the form of the curve, with the equilibrium theory. The following construction gives this curve.

With centre C and radius CA (half the difference of the height at spring and neaps), describe a circle; and in AC produced take CD to CA as 12 to 5. Divide the circumference of the circle into twelve hours, representing the twelve hours of moon's transit; and join D with each of these divisions. The lines thus drawn to the hours will give the heights of high water for each hour of the moon's



transit; a constant quantity being, as before stated, added or subtracted in order to refer the height to the proper zero.

According to the theory, the 0^h or 12^h hour-points would be at A; the ratio of DC to AC would be that of the lunar to the solar tide; and the distances of the hour-points from D would be the heights of high water above mean water. But all these properties are, in the actual cases, modified in a manner which must be noticed.

The tides in these discussions are not referred to the transit of the moon *immediately* preceding, but to some earlier transit, namely, the second, third, fourth or fifth preceding transit; it being found that in this way the accordance with the theory becomes more exact. Thus in the British Channel the tides are referred to the *third* preceding transit; and this extends also to Ireland and to the west coast of England and Scotland. On the east coast of England, in the northern parts, as at Shields, Sunderland, Scarborough and Hull, the *fourth* preceding transit is used; at Harwich, Sheerness and London, the *fifth* (see Table B). But this reference to an earlier transit does not make the highest tide correspond exactly with the hour of transit 0^h or 12^h: and it is found, in the cases which have been included in the present examination, that a displacement of the 0^h point about fifteen minutes from A will best make the theoretical and the observed curves agree with each other.

The ratio of DC to AC is, as has been said, 12 to 5; and this, according to the theory, would be the ratio of the lunar to the solar tide. If this were the case, the spring tide measured above mean water would be 17, and the total spring tide above spring tide low water would be 34. The neap tide in this case would be 7 above mean water, and therefore 24 above spring tide low water. Hence the difference of springs and neaps would be to the height of neaps above low water springs as 10 to 24, a ratio constant for all places.

But in fact, this ratio of the excess of springs to the total height of neaps above low water springs is different at different places: and the observations now under consideration show in some measure the law of this difference. The ratio is smaller when the tide is smaller. This appears from the observations at different places, as arranged by Mr. Ross in the annexed Table A. We have there the following results, taking the means of groups of places according to the amount of tide.

Number of places.	Mean neap tide above spring low water.	Mean excess of spring high water above neap.	Ratio.
	ft. in.	ft. in.	
37	9 3	2 5	38 : 10
40	12 0	3 8	33 : 10
39	17 10	5 9	31 : 10
4	27 0	9 8	28 : 10

Where it appears that the actual ratio approaches to the theoretical ratio in proportion as the amount of tide increases.

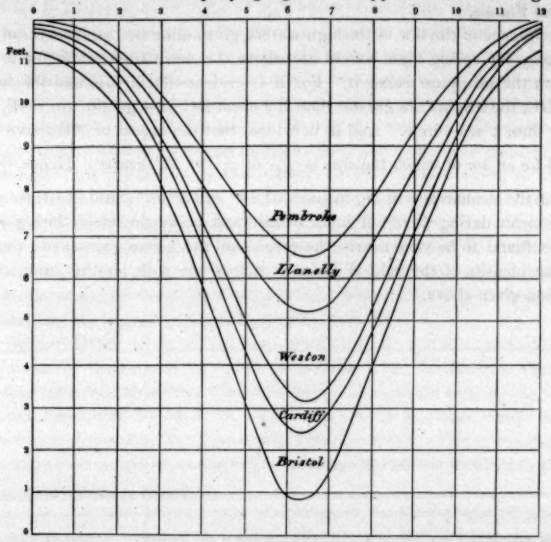
If the ratio just spoken of were constant, we should be able to find the height of

mean water by knowing the excess of springs above neaps: the excess being 10, the mean water would be 7 below the neap high water. But it appears that in general the mean water is lower than this: and the excess of springs being 10, the mean water is from 14 to 19 below neap high water at various points on the coast of Great Britain and France.

In consequence of the law of the high waters, given alike by the theory and by the observations, the spring high waters are above the mean high water for a longer period than the neaps are below it. For it is evident that if DE and DF be each equal to DC, the heights are greater than the mean DC through the arc EAF, which is greater than a semicircle. And it is evident that the excess of AE above a quadrant will be an arc of which the sine is $\frac{1}{2}\frac{EC}{DC}$ or $\frac{5}{24}$; or 12° nearly. Hence the two portions of the semicircle will be, in time, $3^h\ 24^m$ and $2^h\ 38^m$; and the tides will be above the mean during $6^h\ 48^m$ of lunar transit, and below the mean during $5^h\ 12^m$; and this is found to be very nearly the case at all the places examined; thus confirming the identity of the rule of different places one with another, and with the construction given above.

Additional Note on the Tides of the Bristol Channel.

Mr. Ross has traced the modification which the semimensual inequality of heights undergoes in ascending the Bristol Channel from Pembroke to Bristol. This modification is shown in the accompanying figure. It appears from the diagram which



Mr. Ross has drawn from the observations, that the difference of springs and neaps increases gradually from Pembroke to Llanelly, Weston, Cardiff, and finally Bristol, the difference being 5 ft. 6 in. at the first place, and 10 ft. 6 in. at the last; and the curve which represents the change from day to day being at all the places of the same form, namely, of the form described in the preceding paper.

W. W.

Trinity College, Cambridge,
Nov. 3, 1849.

Table A.—Results of Tide Observations arranged according to the amount of excess of Springs above Neaps.

Table B.—Places along the same coasts arranged in the order of their "Establishment."

Table A.

Number of observations from which curves were formed.		"Establishment" of the port.	Mean spring rise above mean low water spring.	Mean neap rise above mean low water spring.	Excess of spring over neap.	
		h m	ft. in.	ft. in.	ft. in.	
128	Ardrishaig	12 0	9 2	8 7	0 7	
704	Lowestoft	9 57	6 6	5 4	1 2	
673	Belfast	10 43	9 5	8 1	1 4	Third preceding transit.
375	Greenock	12 8	9 9	8 2	1 7	Third preceding transit.
107	Ayr Harbour	12 10	8 9	7 2	1 7	
418	Harwich	0 6	11 6	9 9	1 9	Fifth preceding transit.
595	Donaghadee	11 13	11 3	9 5	1 10	
218	Crookhaven	4 9	9 10	8 0	1 10	
190	Baltimore	4 23	10 2	8 3	1 11	
144	Courtmacsherry	4 36	10 8	8 7	2 1	
233	Skull	4 2	9 8	7 7	2 1	
1,059	Kingstown	11 10	11 0	8 10	2 2	Third preceding transit.
209	Castletown	4 14	9 10	7 7	2 3	
351	Peterhead	0 34	10 9	8 6	2 3	
130	Bantry Harbour	3 47	10 2	7 8	2 6	
90	Arcachon, France	4 37	11 8	9 2	2 6	
77	Boucout, France	3 39	8 8	6 1	2 7	
123	Dunmore	5 27	12 3	9 8	2 7	
4,230	Portsmouth	11 41	12 8	10 0	2 8	Third preceding transit.
373	Cork	5 1	11 9	9 1	2 8	Third preceding transit.
51	Castletownsend	4 21	10 9	8 1	2 8	
299	Waterford	6 6	13 5	10 9	2 8	
193	Inverness	12 18	12 2	9 6	2 8	
171	Kinsale	4 43	11 7	8 9	2 10	
522	Sligo	6 0	8 8	5 9	2 11	Third preceding transit.
377	Sheephaven	5 25	11 11	9 0	2 11	
1,383	Ramsgate	11 41	15 6	12 7	2 11	
124	Bordeaux, France	6 50	14 1	11 2	2 11	
4,233	Sheerness	0 37	16 1	13 1	3 0	Fifth preceding transit.
105	Loch Inver	6 41	13 11	10 11	3 0	
69	East Looe	5 26	16 2	13 2	3 0	
446	Inishbofin	5 5	12 10	9 9	3 1	
76	Omonville, France	7 29	15 6	12 5	3 1	
692	Westport	4 57	12 8	9 6	3 2	
92	Peel, Isle of Man	11 8	16 3	13 1	3 2	
103	Caernarvon	9 33	13 9	10 7	3 2	
156	Port Navallo, France	3 42	12 11	9 9	3 2	
183	Tobermorey	5 36	12 10	9 7	3 3	
79	Ramsay, Isle of Man	11 12	19 3	16 0	3 3	
125	Royan, France	3 38	13 3	10 0	3 3	
86	St. Surin, France	4 11	14 3	11 0	3 3	
277	Roundstone	4 28	13 6	10 2	3 4	
117	Goodick Pier	6 56	11 7	8 3	3 4	
937	Dundee	2 32	14 7	11 3	3 4	
125	Patiras, France	5 10	15 6	12 2	3 4	
13,400	London	1 59	19 6	16 1	3 5	Fifth preceding transit.
705	Sunderland	3 22	14 5	11 0	3 5	Fourth preceding transit.
541	Holyhead	10 11	16 0	12 7	3 5	Third preceding transit.
236	Foynes Island, Shannon	5 35	15 5	12 0	3 5	
356	Scarborough	4 11	15 10	12 5	3 5	Fourth preceding transit.
821	Hartlepool	3 28	15 0	11 7	3 5	Fourth preceding transit.
688	Granton Pier	2 20	16 0	12 7	3 5	
	North Shields	3 30	13 8	10 3	3 5	Fourth preceding transit.
148	Socoa, France	3 19	12 3	8 10	3 5	
159	Dunkirk, France	12 8	16 10	13 5	3 5	
2,820	Devonport	5 43	15 5	11 11	3 6	Fourth preceding transit.
2,823	Leith	2 17	16 4	12 9	3 7	Fourth preceding transit.
299	Barfleur, France	8 51	17 0	13 5	3 7	
155	Concarneau, France	3 12	13 1	9 6	3 7	
154	Port Louis, France	3 11	13 1	9 5	3 8	

TABLE A. (Continued.)

Number of observations from which curves were formed.		"Establishment" of the port.	Mean spring rise above mean low water spring.	Mean neap rise above mean low water spring.	Excess of spring over neap.	
		h m	ft. in.	ft. in.	ft. in.	
104	Cordouan Lighthouse, France	3 37	13 10	10 2	3 8	
437	Thurso	8 27	13 3	9 6	3 9	Third preceding transit.
134	Melville, France	9 36	21 1	17 4	3 9	
107	La Hougue, France	8 42	18 5	14 7	3 10	
66	Aberystwyth	7 31	13 5	9 7	3 10	
684	Galway	4 35	14 10	10 11	3 11	Third preceding transit.
164	Belleisle, France	3 18	14 3	10 4	3 11	
147	Calais, France	11 49	19 6	15 7	3 11	
121	Ile d'Yeu	3 6	14 2	10 2	4 0	
125	Pwllheli	7 46	13 8	9 8	4 0	
1,207	Great Grimsby	5 36	19 2	15 1	4 1	
153	Limerick, Shannon	6 20	16 10	12 8	4 2	
194	Tarbert Island, Shannon	4 57	14 6	10 4	4 2	
259	Cherbourg, France	7 49	16 11	12 9	4 2	
134	Havre, France	9 51	22 1	17 11	4 2	
2,116	Dover	11 12	18 8	14 5	4 3	Third preceding transit.
170	Aix Island, France	3 20	16 11	12 8	4 3	
174	St. Nazaire, France	3 40	15 2	10 11	4 3	
154	Beagh Castle, Shannon	5 49	17 6	13 2	4 4	
157	Mellon, Shannon	6 1	18 3	13 10	4 5	
115	Port en Bessin, France	8 57	19 11	15 6	4 5	
703	Hull	6 29	20 10	16 4	4 6	Fourth preceding transit.
118	Alderney	6 46	17 4	12 10	4 6	
258	Douglas, Isle of Man	11 12	20 8	16 1	4 7	
156	Noirmoutier Island, France	3 2	15 11	11 4	4 7	
129	Goury, France	7 6	21 11	17 3	4 8	
153	Cape Grisnez, France	11 27	21 6	16 9	4 9	
223	Tarn Point	11 22	23 1	18 1	5 0	
213	Whitehaven	11 14	23 3	18 2	5 1	
138	Beaumaris	10 32	21 5	16 4	5 1	
132	Fécamp, France	10 44	23 3	18 1	5 2	
513	Brest, France	3 47	19 1	13 10	5 3	Third preceding transit.
62	Honfleur, France	9 29	23 4	18 1	5 3	
13,400	Liverpool	11 16	25 7	20 3	5 4	Third preceding transit.
135	Boulogne, France	11 25	24 10	19 5	5 5	
74	Sein Island, France	3 21	17 6	12 1	5 5	
4,236	Pembroke	6 12	21 0	15 6	5 6	Third preceding transit.
74	Ushant	3 32	19 4	13 9	5 7	
143	Pontasval, France	4 26	22 4	16 8	5 8	
305	Roscoff, France	4 46	23 1	17 4	5 9	
175	Poulton-le-Sands	11 26	27 3	21 6	5 9	
149	Ploumarach, France	5 15	24 3	18 5	5 10	
176	Abervrach, France	4 14	21 9	15 10	5 11	
184	Morlaix Roads, France	4 53	23 9	17 10	5 11	
122	St. Ives	4 44	21 0	15 1	5 11	
72	Ilfracombe	5 42	27 4	21 4	6 0	
221	Dieppe	11 6	27 0	20 8	6 4	
303	Fleetwood	11 12	26 3	19 8	6 7	
292	Port des Enfans, France	5 17	25 5	18 10	6 7	
117	Cayeux, France	11 5	27 6	20 11	6 7	
391	Brehat, France	5 51	31 2	23 7	7 7	
81	Lezardrieux, France	5 54	30 3	22 2	8 1	
119	Jersey	6 15	29 9	21 5	8 4	
370	Weston-super-Mare	6 54	37 3	28 9	8 6	Third preceding transit.
129	Ecrehou	6 32	30 11	22 5	8 6	
139	Erqui	5 59	33 3	24 5	8 10	
153	St. Malo, France	6 5	35 0	25 10	9 2	
277	Chausey, France	6 9	35 2	25 10	9 4	
294	Granville, France	6 13	37 1	27 2	9 11	
138	Portishead	7 11	41 4	31 1	10 3	

Table B.

	Establishment.
	h m
From the Land's End to Ramsgate.	
East Looe	5 26
Devonport (4th transit?)	5 43
Portsmouth (3rd transit)	11 41
Dover (3)	11 12
Ramsgate	11 41
From the Land's End up St. George's Channel round the North of Scotland to London.	
St. Ives	4 44
Ilfracombe	5 42
Weston-super-Mare (3)	6 54
Portishead	7 11
Pembroke (3)	6 12
Goodick Pier	6 56
Aberystwyth	7 31
Pwllheli	7 46
Caernarvon	9 33
Holyhead	10 11
Beaumaris	10 32
Liverpool (3)	11 16
Fleetwood	11 12
Tarn Point	11 22
Poulton-le-Sands	11 26
Peel, Isle of Man	11 8
Douglas, Isle of Man	11 12
Ramsay, Isle of Man	11 12
Whitehaven	11 14
Ayr	12 10
Greenock (3)	12 8
Thurso (3)	8 27
Inverness	12 18
Peterhead	0 34
Dundee	2 32
Granton (4)	2 20
Leith	2 17
North Shields (4)	3 30
Sunderland (4)	3 22
Hartlepool	3 28
Scarborough (4)	4 11
Hull (4)	6 29
Great Grimsby	5 36
Lowestoft	9 57
Harwich (5)	0 6
Sheerness (5)	0 37
London (5)	1 59
From Bantry Bay up St. George's Channel round the North of Ireland to the Shannon.	
Bantry Harbour	3 47
Castletown (Berehaven)	4 14
Skull	4 2
Crookhaven	4 9
Baltimore	4 23
Castletownsend	4 21
Courtmacsherry	4 36
Kinsale	4 43
Cork (3)	5 1
Dunmore	5 27
Waterford	6 6
Kingstown (3)	11 10
Donaghadee	11 13
Belfast (3)	10 43
Sheephaven	5 25
Sligo (3)	6 0
Westport	4 57
Inishbofin	5 5
Roundstone	4 28
Galway (3)	4 35
Tarbert, Shannon	4 57
Foynes Island, Shannon	5 35
Beagh Castle, Shannon	5 49
Mallon, Shannon	6 1
Limerick, Shannon	6 20
From Arcachon in the Bay of Biscay to Dunkirk.	
Arcachon	4 37
Bordeaux	6 50
St. Surin	4 11
Royan	3 38
Cordouan	3 27
Ile d'Aix	3 20
Ile d'Yeu	3 6
Noirmoutier Island	3 2
St. Nazaire	3 40
Belleisle	3 18
Port Louis	3 11
Concarneau	3 12
Brest (3)	3 47
Ushant	3 32
Morlaix Roads	4 53
Brehat	5 51
Erqui	5 59
St. Malo	6 5
Granville	6 13
Chausey	6 9
Jersey	6 15
Ecrehou	6 32
Alderney	6 46
Cherbourg	7 49
Barfleur	8 51
La Hougue	8 42
Honfleur	9 29
Havre	9 51
Fécamp	10 44
Dieppe	11 6
Cayeux	11 5
Boulogne	11 25
Cape Grisnez	11 27
Calais	11 49
Dunkirk	12 8

For the places not otherwise marked in these Tables, the tides were referred to the transit immediately preceding, as giving sufficient exactness for general maritime purposes: but observations received at the Admiralty since the above laws were discovered, have been referred to the third, fourth, or fifth preceding transit, according to their place in Table B.

The Devonport tides discussed some years ago, apart from those of neighbouring places, appeared to give the greatest exactness with the *fourth* preceding transit, which has accordingly been used in the Admiralty Tables. There can be no doubt at present that the *third* preceding transit is more correct for this port; but the labour of recalculating new Tables would be great, and the difference of the result would never be more than one minute in the time and one inch in the height.

XII. *Experiments and Observations upon the Properties of Light.*

By Lord BROUGHAM, *F.R.S.*,
Member of the National Institute, and of the Royal Academy of Naples.

Received November 6, 1849,—Read January 10, 1850.

THE optical inquiries of which I am about to give an account, were conducted at this place in the months of November and December 1848, and continued in autumn 1849 at Brougham, where the sun proved of course much less favourable than in Provence: they were further prosecuted in October. I had thus an opportunity of carefully reconsidering the conclusions at which I had originally arrived; of subjecting them first to analytical investigation, and afterwards to repetition and variation of the experiments; and of conferring with my brethren of the Royal Society and of the National Institute. The climate of Provence is singularly adapted to such studies. I find, by my journal of 1848, that during forty-six days which I spent in those experiments, from 8 A.M. to 3 P.M., I scarcely ever was interrupted by a cloud, although it was November and December*. I have since had the great benefit of a most excellent set of instruments made by M. SOLEIL of Paris, whose great ingenuity and profound knowledge of optical subjects can only be exceeded by his admirable workmanship. I ought however to observe, that although his heliostate is of great convenience in some experiments, it yet is subject (as all heliostates must be) to the imperfection of losing light by reflexion, and consequently I have generally been obliged to encounter the inconvenience of the motion of the sun's image, especially when I had to work with small pencils of light. This inconvenience is materially lessened by using horizontal prisms and plates.

Although I have made mention of the apparatus of great delicacy which I employed, it must be observed that this is only required for experiments of a kind to depend upon nice measurements. All the principles which I have to state as the result of my experiments in this paper, can be made with the most simple apparatus, and without any difficulty or expense, as will presently appear.

It is perhaps unnecessary to make an apology for the form of definitions and propositions into which my statement is thrown. This is adopted for the purpose of making the narrative shorter and more distinct, and of subjecting my doctrines to a fuller scrutiny. I must further premise that I purposely avoid all arguments and

* Of seventy-eight days of winter in 1849, I had here only five of cloudy weather. Of sixty-one days of summer at Brougham, I had but three or four of clear weather; one of these fortunately happened whilst Sir D. BREWSTER was with me, and he saw the more important experiments.

suggestions upon the two rival theories—the Newtonian or Atomic, and the Undulatory. The conclusions at which I have arrived are wholly independent, as it appears to me, of that controversy. I cautiously avoid giving any opinion upon it; and instead of belonging to the sect of undulationists or anti-undulationists, I incline to agree with my learned and eminent colleague M. Biot, who considers himself as a "*Rieniste*," and neither "ondulationiste" nor "anti-ondulationiste."

Chateau Eleanor-Louise (*Provence*)*,
1*st November* 1849.

Definitions.

1. *Flexion* is the bending of the rays of light out of their course in passing near bodies. This has been sometimes termed *diffraction*, but *flexion* is the better word.

2. Flexion is of two kinds—*inflexion*, or the bending towards the body; *deflexion*, or the bending from the body.

3. *Flexibility*, *deflexibility*, *inflexibility*, express the disposition of the homogeneous or colour-making rays to be bent, deflected, inflected by bodies near which they pass.

Although there is always presumed to be a flexion and a separation of the most flexible rays from the least flexible (the red from the violet for example) when they pass by bodies, yet the compound rays are not so presumed to be decomposed when reflected by bodies. This is probably owing to the successive inflexions and deflexions before and after reflexion, correcting each other and making the whole beam continue parallel and undecomposed instead of becoming divergent and being decomposed.

Proposition I.

The flexion of any pencil or beam, whether of white or of homogeneous light, is in some constant proportion to the breadth of the coloured fringes formed by the rays after passing by the bending body. Those fringes are not three, but a very great number, continually decreasing as they recede from the bending body, in deflexion, where only one body is acting; and they are real images of the luminous body by whose light they are formed.

Exp. 1. If an edge be placed in a beam or in a pencil of white light, fringes are formed outside the shadow of the edge and parallel to it, by deflexion. They are seen distinctly to be coloured, the red being furthest from the shadow, the violet nearest, the green in the middle between the red and the violet. The best way to observe this is to receive the light on an instrument composed of two vertical and two horizontal plates, each moving by a screw so as to increase or lessen the distance

* In experiments at this place, in winter, I found one great advantage, namely, the more horizontal direction of the rays. In summer they are so nearly vertical, that a mirror must be used to obtain a long beam or pencil, which is often required in these experiments, and so the loss of light countervails the greater strength of the summer sun's light.

between the opposite edges. a, a' are (Plate X. fig. 1) the vertical, b, b' the horizontal edges, s, s' are the screws; and these may be fitted with micrometers, so as to measure very minute distances of the edges by graduated scales B B', B' C. For the purpose of the present proposition the aperture only needs be considered, of about a quarter of an inch square. The light passing through this aperture is received on a chart placed first one foot, and then several feet from the instrument. The fringes are increased in breadth by inclining the chart till it is horizontal, or nearly so, when the fringes parallel to b, b' are to be examined, and holding it inclined laterally when the fringes parallel to a, a' are to be examined. It is also convenient to let the white light beyond the fringes pass through; and for this purpose, a'', b'' being the figure of the instrument (fig. 2), and the light received on the chart, a hole may be made in its centre $o\ p\ q$, through which the greater portion of the white light may be suffered to pass. The fringes are plainly seen to run parallel to the edges forming them; as $o\ p$ parallel to b'' and $p\ q$ parallel to a''. The reddish is furthest from the shadow, the bluish nearest that shadow; also the fringe nearest the shadow is the broadest, the rest decrease as they recede from the shadow into the white light of the disc. Sometimes it is convenient to receive the fringes on a ground glass plate, and to place the eye behind it. They are thus rendered more perceptible.

When the edges are placed in homogeneous light, they are all of the colour which passes by any edge; and two diversities are here to be noted carefully. *First*, the fringes made by the red light are broader than those made by any of the other rays, and the violet are the narrowest, the intermediate fringes being of intermediate breadths. *Second*, the fringes made by the red are furthest from the direct rays, the violet nearest those rays, the intermediate at intermediate distances. This is plainly shown in the following experiment.

Exp. 2. In fig. 3, C represents the image of the aperture when the rays of the prismatic spectrum are made to pass through it. But instead of making the fringes by a single edge deflecting, and so casting them in the spectrum, I approach the opposite edges, so that both acting together on the light, the fringes are seen in the shadow and surrounding the spectrum. These fringes are no longer parallel to the shadows of the edges as they were in the white light, but incline towards the most refrangible and least flexible rays, and away from the least refrangible and most flexible. Thus the red part r of the fringes is nearest the shadow of the edge a'; the orange, o, next; then yellow, y; green, g; blue, b; indigo, i; and violet, v. Moreover, the fringe $r\ v$ is both inclined in this manner, so that its axis is inclined, and also its breadth increases gradually from v to r. This is a complete refutation of the notion entertained by some that Sir I. Newton's experiment of measuring the breadths in different coloured lights and finding the red broadest, the violet narrowest, explains the colours of the fringes made in white light as if these were only owing to the different breadths of the fringes formed by the different rays. The present experiment clearly proves, that not only the fringes are broadest in the least refrangible rays, but

those rays are bent most out of their course, because both the axis of the fringes is inclined, and also their breadths are various.

Exp. 3. Though called by GRIMALDI, the discoverer, the three fringes, as well as by NEWTON and others who followed him, they are seen to be almost innumerable, if viewed through a prism to refract away the scattered light that obscures them. I stated this fact many years ago*.

Exp. 4. That the fringes are images may be at once perceived, not when formed in the light disc as in some of the foregoing experiments, but when formed in the shadow. Thus when the opposite edges are moved so near one another as to form fringes bordering the luminous body's image, they are formed like the disc they surround. When you view a candle through the interval of the opposite edges, you perceive that the fringes are images of its flame, with the wick, and that they move as the flame moves to and fro. When you observe the half-moon in like manner, you perceive that the side of the fringes answering to the rectilinear side of the moon, are rectilinear, and the other side circular; and when the full moon is thus viewed, the fringes on both sides are circular. The circular disc of the moon is, indeed, drawn or elongated as well as coloured. It is, that is to say, the fringe or image is exactly a spectrum by flexion. Like the prismatic spectrum, it is oblong, not circular, and it is coloured; only that its colours are much less vivid than those of the prismatic spectrum.

PROPOSITION II.

The rays of light, when inflected by bodies near which they pass, are thrown into a condition or state which disposes them to be on one of their sides more easily deflected than they were before the first flexion; and disposes them on the other side to be less easily deflected: and when deflected by bodies, they are thrown into a condition or state which disposes them on one side to be more easily inflected, and on the other side to be less easily inflected than they were before the first flexion.

Let RA (fig. 4) be a ray of light whose opposite sides are R A, R′ A′, and let A be a bending edge near which the ray passes, the side R′ A′ acquires by A's inflexion, a disposition to be more easily deflected by another body placed between A and the chart C, and the side R A acquires a disposition to be less easily deflected than before its first flexion; and in like manner R′ A′ acquires a disposition to be more easily inflected, and R A a disposition to be less easily inflected by a body placed between A and C.

Exp. 1. Place A′ (fig. 5) in any position between A and $v r$, the image made on C by A's influence, as at A′ or A″, or close to A at A‴. If it is placed on the same side of the ray with A, no difference whatever can be perceived to be made on the breadth of $r v$, or on its distance v R′ from the direct ray R R′. In like manner the image by deflexion $r' v'$ is not affected at all, either in its breadth, or in its removal from R R′ by any object, a, a', placed on the same side with A of the deflected ray A v'.

* Philosophical Transactions, 1797, Part II.

But (fig. 6) place B anywhere between A and $v r$ on the side of the ray opposite to A, and the breadth of $r v$ is increased, and also its distance from the direct ray R R′, as $v' r'$; and in like manner (fig. 7) the deflected rays A v, A r are both more separated, making a broader image at $r'' v''$, and are further removed from RR′ by B's inflexion.

Exp. 2. If you bend the rays either by a single edge, or by the joint action of two edges, it makes not the least difference either in the breadth or in the distance from the direct rays of the images, or in the distension or elongation of the luminous body's disc, whether the bending body is a perfectly sharp edge (which in regard to the rays of light is a surface, though a narrow one), or is a plane (that is, a broader surface), or is a curve surface of a very small, or of a very large radius of curvature.

In fig. 8, $a e$ is an instrument composed of four pieces of different forms, but all in a perfectly straight line; $a b$ is an extremely sharp edge; $b c$ a flat surface; $c d$ a cylindrical or circular surface of a great radius of curvature; $d e$ one of a small radius of curvature. But all these pieces are so placed that E $\delta \gamma$ is a tangent to $e d$, $d c$, and is a continuation of $\gamma \beta$ K, that is, of $c b$, $b a$. So the light passing by the whole $a b c d e$, passes by one straight line E K, uniting or joining the four surfaces. It is found that the image or fringe I I′, made by $a b c d e$ (or E $\delta \gamma \beta$ K), is of the same breadth and in the same position throughout its whole length. So if directly opposite to this edge another straight edge is placed, and acts together with $a b c d e$ on the light passing, the breadth of the fringe I is increased, and its distance is increased from the direct rays, but it has the exact same breadth from I to I′; its portion I′ q answering to $a b$, q P answering to $b c$, P O answering to $c d$, and O I answering to $d e$, are of the same breadth, provided care be taken that the second edge is exactly parallel to the edge E K. And this experiment may be made with the second edge behind $a b c d e$, as in Exp. 1 of this proposition; also it may be usefully varied by having the second edge composed of four surfaces like the first, only it becomes the more necessary to see that this compound edge is accurately made and kept quite parallel to the first, any deviation, however minute, greatly affecting the result. When care is thus used the fringes are as in $r v$, $v' r'$, quite the same in breadth and in position through their whole length; and not the least difference is to be discerned in them, whether made by a second edge, which is one sharp edge, or by a compound second edge, similar to $a b c d e$.

Hence I conclude that the beam passing by the compound edge, or compound edges, is exactly as much distended by the different flexibility of the rays, and is exactly as much bent from its direct course when the flexion is performed by a sharp edge, by a plane surface, by a very flat cylinder, or by a very convex cylinder; and therefore that all the action of the body on the rays is exercised by one line, or one particle, and not first by one and then by others in succession; and this clearly proves that after a first flexion takes place, no other flexion is made by the body on the same side of the rays. This is easily shown.

For a plane surface is a series or succession of edges infinitely near each other;

and a curve surface in like manner is a succession of infinitely small and near plane surfaces or edges. Let *a b* (fig. 9) be the section of such a curve surface. The particle P coming first near enough the ray R R′ to bend it, then the next particle O is only further distant from R R′, the unbent ray, than the particle P by the versed sine of the infinitely small arch O P. But O is not at all further distant than P from the ray bent by P into *q r*, and yet we see that O produces no effect whatever on the ray after P has once bent it. No more do any of the other particles within whose spheres of flexion the ray bent by P passes. The deflected ray *q r′* no doubt is somewhat more distant from O than the incident ray was from P, but not so far as to be beyond O's sphere of deflexion; for O acts so as to make the other fringes at greater distances than the first. Consequently O could act on the first fringe made by P as much as P can in making the second, third, and other fringes; and if this be true of a curve surface, it is still more so of a plane surface; all whose particles are clearly equidistant from the ray's original path, and the particles after the first are in consequence of that first particle's flexion nearer the bent ray, at least in the case of inflexion. But it is to be observed, moreover, that in the experiment with two opposite edges, inflexion enters as well as deflexion, and consequently this demonstration, founded on the exact equality of the fringes made by compound double edges, appears to be conclusive. For it must be observed that this experiment of the different edges and surfaces, plane and curve, having precisely the same action, is identical with the former experiment of two edges being placed one behind the other, and the second producing no effect if placed on the same side of the ray with the first edge. These two edges are exactly like two successive particles of the same surface near to which the rays pass. Consequently the two experiments are not similar but identical; and thus the known fact of the edge and the back of a razor making the same fringes, proves the polarization of the rays on one side. Thus the proposition is proved as to polarization.

Exp. 3. The proposition is further demonstrated, as regards disposition, in the clearest manner by observing the effect of two bodies, as edges, whether placed directly opposite to each other while the rays pass between them so near as to be bent, or placed one behind the other but on opposite sides of the rays. Suppose the edges directly opposite one to the other, and suppose there is no disposition of the rays to be more easily bent by the one edge in consequence of the other edge's action. Then the breadth and distension and removal of the fringes caused by the two edges acting jointly, would be in proportion to the sum of the two separate actions. Suppose that one edge deflects and the other inflects, and suppose that inflexion and deflexion are equal at equal distances, following the same law; then the force exerted by each edge being equal to *d*, that exerted by both must be equal to 2 *d*. But instead of this we find it equal to 5*d*, or 6*d*, which must be owing to the action of the two introducing a new power, or inducing a new disposition on the rays beyond what the action of one did.

If, however, we would take the forces more correctly (fig. 10), let A and B be the two edges, and let their spheres of flexion be equal, AC($=a$) being A's sphere of inflexion and B's sphere of deflexion; BC ($=a$) being A's sphere of deflexion and B's sphere of inflexion; and let the flexion in each case be inversely as the mth power of the distance. Let CP$=x$, PM$=y$, the force acting on a ray at the distance $a+x$ from A and $a-x$ from B. Then if B is removed and only A acts, $y=\frac{1}{(a+x)^m}$. If B also acts, $y'=\frac{1}{(a+x)^m}+\frac{1}{(a-x)^m}$.

Now the loci of y and y' are different curves, one similar to a conic hyperbola, the other similar to a cubic; but of some such form when $m=1$, as SS' and TT'. It is evident that the proportion of $y:y'$ can never be the same at any two points, and consequently that the breadths of the fringes made by the action of one can never bear the same proportion to the breadths of those made by the action of both, unless we introduce some other power as an element in the equation, some power whereby from both values, y and y', x may disappear, else any given proportion of $y:y'$ can only exist at some one value of x. Thus suppose (which the fact is) $y:y'::1:5$ or $1:6$, say $::1:6$, this proportion could only hold when

$$x=\frac{\left(5^{\frac{1}{m}}-1\right)a}{5^{\frac{1}{m}}+1} \text{ or } =\frac{\left(4^{\frac{1}{m}}-1\right)a}{4^{\frac{1}{m}}+1}, \text{ if } y:y'::1:5.$$

When $m=2$, the force being inversely as the square of the distance, then $x=\frac{a}{3}$ and $x=\frac{(\sqrt{5}-1)}{\sqrt{5}+1}a$, are the values at which alone $y:y'::1:5$ and $1:6$ respectively.

But this is wholly inconsistent with all the experiments; for all of these give nearly the same proportion of $y:y'$ without regard to the distance, consequently the new element must be introduced to reconcile this fact. Thus we can easily suppose the conditions, *disposition* and *polarization* (I use the latter term merely because the effect of the first edge resembles polarization, and I use it without giving any opinion as to its identity), to satisfy the equation by introducing into the value of y some function of $a-x$. But that the joint action of the two edges never can account for the difference produced on the fringes, is manifest from hence, that whatever value we give to m, we find the proportion of $y':y$ when $x=0$ only that of double, whereas 5 or 6 times is the fact. The same reasoning holds in the case of the spheres of flexion being of different extent; and there are other arguments arising from the analysis on this head, which it would be superfluous to go through, because what is delivered above enables any one to pursue the subject. The demonstration also holds if we suppose the deflective force to act as $\frac{1}{n}$ of the distance, while that of inflexion acts as $\frac{1}{m}$. But I have taken $m=n$ as simpler, and also as more probably the fact.

I have said that the rays become less easily inflected and deflected; but it is plain

that on the polarized side they are not inflected or deflected at all. Their disposition on the opposite side is a matter of degree; their polarization is absolnte and their flexion null.

Proposition III.

The rays disposed on one side by the first flexion are polarized on that side by the second flexion, and the rays polarized on the other side by the first flexion are depolarized and disposed on that side by the second flexion.

This proposition is proved by carefully applying the first experiment of Prop. II.; but great care is required in this experiment, because when three edges are used consecutively, the third edge often appears to act on rays previously acted on by both the other two, when it is only acting on those previously acted on by one or other of those two. Thus when edge A has inflected and edge B afterwards deflects the rays disposed by A, a third edge C may, when applied on the side opposite to B, seem to increase the flexion, and yet on removing A altogether we may find the same effect continue, which proves that the only action exercised had been by B and C, and that C had not acted on rays previously bent by both A and B, which the experiment of course requires to prove the proposition. I was for a long while kept in great uncertainty by this circumstance, whether the third edge ever acted at all. That it never acted on the side of the ray on which the second edge acted, I plainly saw; but I frequently changed my opinion whether or not it acted on the opposite side, that is, on the same side with the first edge. Nor could I confidently determine this important point until I had the benefit of an instrument which I contrived for the purpose, and which, executed by M. Soleil, enabled me satisfactorily to perform the *experimentum crucis* as follows:—

In fig. X. A B is a beam, on a groove (of which the sides are graduated) three uprights are placed, the one, B, fixed, the other two, C and D, moving in the groove

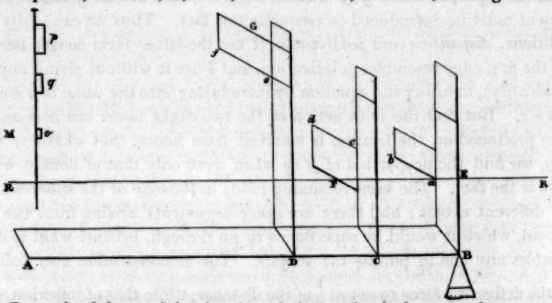


fig. X.

of A B. On each of the uprights is a broad sharp-edged plate, moving up and down the upright by a rack and pinion, so that both the plates F, G could be approached as near as possible to each other, and so could F be approached to the plate E on the

fixed upright B; while also each of the three plates could be brought as near the rays that passed as was required; and so could each be brought as near the opposite edge of the neighbouring plate. It is quite necessary that this instrument should be heavy in order to give it solidity; it is equally necessary that the rack and pinion movement should be just and also easy; for the object is to fix the plates at will, so that their position in respect of the rays may be easily changed, and when once adjusted may be immovable until the observer desires to change their position.

The light was passed under the plate E and acted upon by *a b*, its lower edge. The second plate E was then raised on C so as to act on the side of the rays opposite to *a b*, by its upper edge *c d*. The fringes inflected by *a b* were thus deflected by *c d*, in virtue of the disposition given to the side next *c d*. Then the third plate G, on its stand D, was moved so that it could be brought to act by its lower edge *e f*, which was approached to the rays deflected by *c d*, and placed on their opposite side. The action was observed by examining the fringes on the chart M. Those which had been as *o*, made by the joint action of the two first edges E, F, were seen to move upwards to *p* as the third edge G came near the rays; and *p* was both broader than *o*, and further removed from the direct rays R R′. In order to make quite sure that this change in the size and position of *o* had not been occasioned by the mere action of two plates, as E and G or F and G, it was quite necessary to remove first E, by drawing it up the stand B. If the fringe *p* then vanished, complete proof was afforded that E had acted as well as G. Then F was removed, and if *p* vanished, proof was afforded that F acted as well as E and G. A very convenient variation of the experiment was also continued and was found satisfactory. When the joint action of F and G gave a fringe, as at *q*, E being removed up the stand B, then E was gently moved down that stand, and as it approached the pencil, which was on its way to F and G, you plainly perceived the fringe enlarged and removed from *q* to *p*. These experiments were therefore quite crucial, and demonstrated that all the edges had concurred to form the fringe at *p*, the first and third inflecting, the second de flecting.

The same experiments were made on the fringes formed by the deflexion of the first edge and the inflexion of the second, and the deflexion of the third.

It is thus perfectly clear that the rays bent by the first edge and disposed on their side opposite to that edge, are bent in the other direction by the second edge acting on that opposite side, and are afterwards again bent in the direction of the first bending by the action of the third edge upon the side which was opposite the second edge and nearest the first edge. But this side is the one polarized by the first edge, and therefore that side is depolarized by the action of the second edge. Hence it is proved that the rays polarized by one flexion are depolarized by a second; and as it is proved by repeated experiments that no body placed on the same side of the rays with any of the bending bodies, whether the first or the second or the third, exercises any action on those rays, it is thus manifest that any one flexion having

disposed, a second polarizes the disposed side; and that any one flexion having polarized, a second flexion depolarizes and disposes the polarized side.

Exp. 3. Another test may be applied to this subject. Instead of a rectilinear edge, I made use of edges formed into a curve, as in fig. 12, where C is such an edge, and then the figure made is $g\,h$, corresponding to the curve $e\,b$. The first edge in the last experiment being formed like C, instead of a straight-lined edge, we can at once perceive that it has acted on the rays as well as the second and third edges, because these being straight-lined, never could give the comb-like shape $g\,h$ to the fringes. This completely confirmed the other observations, and made the inference irresistible.

Proposition IV.

The disposition communicated by the flexion to the rays is alternative; and after inflexion they cannot be again inflected on either side; nor after deflexion can they be deflected. But they may be deflected after inflexion and inflected after deflexion, by another body acting upon the sides disposed, and not by its acting upon the sides polarized.

This is gathered from the experiments in proof of the second and third propositions.

Proposition V.

The disposition impressed upon the rays, whether to be easily deflected or easily inflected by a second bending body, is strongest nearest the first bending body, and decreases as the distance between the two bodies increases.

Plate XI. fig. 11. Let $A\,B=a$ be the distance between the first bending body and a given point, more or less arbitrarily assumed; P the second body; $A\,P=x$; $P\,M=y$, the force exerted by the second body at P; C= the chart; $P\,M=y$ is in some inverse proportion to A P, but not as $\frac{1}{A\,P^m}$ or $\frac{1}{x^m}$, because it is not infinite at A, but of an assignable value there; therefore $y=\frac{1}{(a+x)^m}$; and the curve which is the locus of P has an asymptote at B, when $x=-a$. The fringes being received on the chart at C, it might be supposed that the difference in their breadth, by which I measure the force, or y, is owing to P approaching the chart C, in proportion as it recedes from A, and thus making the divergence less in the same proportion; but the experiments are wholly at variance with this supposition.

Exp. 1. The following table is the result of one such experiment. The first column contains the distances horizontally of P from A, being the sines of the angle made by the rays with the vertical edges; the second column contains the real distance of the second from the first edge, the secant of that angle; the third column gives the breadths of the fringes at the distances given in the preceding columns; the fourth gives the values of y, supposing M N were a conic hyperbola.

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Sines.	Secants.	Real value of y.	Hyperbolic value.
20	35	$3\frac{1}{2}$	$3\frac{1}{2}$
65	85	$1\frac{4}{5}$	$1\frac{4}{5}$
85	$107\frac{1}{2}$	$1\frac{1}{4}$	$1\frac{1}{4}$
195	240	$0\frac{4}{5}$	$0\frac{4}{5}$

The unit here is $\frac{1}{10}$th of an inch.

It is plain that this agrees nearly with the conic hyperbola, but in no respect with a straight line; and upon calculating what effect the approach of P to C would have had, nothing could be more at variance with these numbers. But

Exp. 2. All doubt on this head is removed by making P the fixed point, and moving the first edge A nearer or further from it. In this experiment, the disturbing cause, arising from the varying distance from the chart, is entirely removed; and it is uniformly found that the decrease in the force varies notwithstanding with the increase of the distance. I have here only given the measures by way of illustration, and not in order to prove what the locus of y (or P) is, or, in other words, what the value of m is.

Exp. 3. When one plate with a rectilinear edge is placed in the rays, and a second such plate is placed at any distance between it and the chart, the fringes are of equal breadth throughout their length, and all equally removed from the direct rays, each point of the second edge being at the same distance from the corresponding point of the first. But let the second plate be placed at an angle with the first, and the fringes are very different. It is better to let the second be parallel to the chart, and to incline the first; for thus the different points of the fringes are at the same distance from the edge which bends the disposed rays. In fig. 13, B is the second plate, parallel to the chart C; A is the first plate; all the points of B, from D to E, are equidistant from C; therefore nothing can be ascribed to the divergence of the bent rays. B bends the rays disposed by A at different distances D D′ and E E′ from the point of disposition. The fringe is now of various breadths from $d\,d'$ to e, the broadest part being that answering to the smallest distance of D, the point of flexion, from D′ the point of disposition; the narrowest part, e, answering to E E′, or the greatest distance of the point of flexion from the point of disposition. Moreover, the whole fringe is now inclined; it is in the form of a curve from $d\,d'$ to e, and the broad part $d\,d'$, formed by the flexion nearest the disposition, is furthest removed from the direct rays; the narrowest part, e, is nearest these direct rays. It is thus quite clear that the flexion by B is in some inverse proportion to the distance at which the rays are bent by B from the point where they were disposed by A. I repeatedly examined the curve $d\,e$, and found it certainly to be the conic hyperbola. Therefore $m=1$, and the equation to the force of disposition is $y=\frac{1}{x}$.

In order to ascertain the value of m, I was not satisfied with ordinary admeasurements, but had an instrument made of great accuracy and even delicacy. It con-

sisted of two plates, A and B (Plate VI.), with sharp rectilinear edges, one, A, horizontal, the other, B, moving vertically on a pivot, and both nicely graduated. The angle at which the second plate was vertically inclined to the first, was likewise ascertained by a vertical graduated quadrant E. Moreover the edges moved also horizontally, and their angle with each other was measured by a horizontal graduated quadrant K. There was a fine micrometer F to ascertain the distances of the two edges from each other, and another to measure the breadth of the fringes on the chart. The observations made with this instrument gave me undoubted assurance that the equation to the curve M N in fig. 11 is $yx=a$, a conic hyperbola, and that the disposing force is inversely as the distance at which the flexion of the rays bent and disposed takes place.

Scholium.—It is clear that the extraordinary property we have now been examining, has no connexion with the different breadths of the pencils at different distances from the point of the first flexion, owing to the divergence caused by that flexion.

By the same kind of analysis, which we shall use in demonstrating the 6th Proposition, it may be shown,—*first*, that the divergence of the rays alone would give a different result, the fringes made by an inflexion following a deflexion and those made by a deflexion following an inflexion; *secondly*, that in no case would the equation to the disposing force be the conic hyperbola, even where that fringe decreased with the increase of the distance; *thirdly*, even where the effect of increasing the distance is such as the dispersion would lead to expect, the rate of decrease of the fringes is very much greater in fact than that calculation would lead to, five or six times as great in many cases; and *lastly*, that instead of the law of decrease being uniform, it would, if caused by the dispersion, vary at different distances from the two edges*. Nothing therefore can be more manifest than that the phenomena in question depend upon a peculiar property of the rays, which makes them change in their disposition with the length of the space through which they have travelled.

It should seem that light may be compared, when bent and thereby disposed, to a body in its nascent state, which, as we find by constant experience, has properties different from those which it has afterwards; and I have therefore contrived some experiments for the purpose of ascertaining whether or not light at the moment of its production (by artificial means) has properties other than those which it possesses after it has been some time produced. This will form the subject of a future inquiry. I would suggest, however, at present that the electric fluid ought to be examined with a view to find whether or not it has any property analogous to disposition, that is, whether it becomes more difficultly attracted at some distance from its evolution, as light is more difficultly bent at a distance from the point of its being disposed. On heat a like experiment may be made. The thermometer would no doubt stand at a different height at different distances from the source of the heat; but the question

* I have given demonstrations of these propositions in a memoir presented to the National Institute, but I am reluctant to load the present paper with them.

is if it will not reach its full height, whatever that may be, more quickly near its source than far from it. This experiment ought above all to be made on radiant heat, in which I confidently expect a property will be found similar to the disposition of light. It is also plain that we may expect strong analogies in magnetism and electro-magnetism.—I throw out these things because my time for such investigations may not be sufficiently extended to let me undertake them with success.

Proposition VI.

The figures made by the inflexion of the second body acting upon the rays deflected by the first, must, according to the calculus applied to the case, be broader than those made by the second body deflecting those rays inflected by the first.

In fig. 14, let A v' be the violet rays and A r' the red, inflected by A and deflected by B. Let A r be the red and A v the violet deflected by A and inflected by B. The action of B must inflect A r, A v into a broader fringe F, than the action of B deflects A v', A r' into the fringe f.

Let B $r=a$ be the distance at which B acts on A r; $rv=d$ be the divergence of the red and violet; c be the distance of the two bent pencils, and $v'r'$ the divergence of the inflected pencil, equal also to d, because we may take the different inflexibility to be as the different deflexibility. B acts on the red of A r v as $\frac{r}{a^m}$; on the violet as $\frac{v}{(a+d)^m}$; and so on A v' as $\frac{v}{(a+d+c)^m}$; on A r' as $\frac{r}{(a+2d+c)^m}$. It is evident that the action in bending A r, A v, or the fringe made by that action, is to the fringe made by the action on A r', A v', as $\frac{r}{a^m}-\frac{v}{(a+d)^m}$: $\frac{r}{(a+2d+c)^m}-\frac{v}{(a+d+c)^m}$; and ultimately the two actions (or sets of fringes) are (supposing $a=1$ and d also $=1$, for simplifying the expression) as

$$2^m\times r\,(3+c)^m\,(2+c)^m-v\,(3+c)^m\,(2+c)^m \text{ to } 2^m r\,(2+c)^m-2^m v\,(3+c)^m.$$

Now the former of these expressions must always be greater than the latter, because $(3+c)^m>1$, and also $(3+c)^m-1>(2+c)^m-1$; and this whatever be the value of m and of c, and whatever proportion we allow of r to v, the flexibilities. But it is also manifest that the excess of the first expression above the second will be greater if the flexibility of the red exceed that of the violet, or if r is greater than v, as $2v$. Hence we conclude; *first*, that in mixed or white light the fringes inflected by B after deflexion by A are greater than those deflected by B after inflexion by A; *secondly*, that they are also greater in homogeneous light; *thirdly*, that the excess of the inflected fringes over the deflected is greater in mixed than in homogeneous light.

The action of flexion after disposition is so much greater than that of simple flexion, that I have only taken into the calculation the compound flexion. But the most accurate analysis is that which makes the two fringes as

$$D+\frac{r}{a^m}-\frac{v}{(a+d)^m} \text{ to } D+\frac{r}{(a+2d+c)^m}-\frac{v}{(a+d+c)^m},$$

D being the breadth of the fringes on the chart by simple flexion in case the rays had passed on without disposition and without a second flexion. If it be carefully kept in mind that D is much less than $\frac{r}{a^m}$, or even $\frac{r}{(a+2d+c)^m}$, and that d is still less than D, then it will always be certain that the first quantity is larger than the second.

Cor.—It is a corollary to this proposition that the difference of the two sets of fringes is increased by the disposition communicated by the rays in passing by the first body. For the excess of the value of r over that of v being increased, the difference between the two expressions is increased.

Proposition VII.

When one body only acts upon the rays, it must, by deflexion, form them into fringes or images decreasing as the distance from the bending body increases. But when the rays deflected and disposed by one body are afterwards inflected by a second body, the fringes will increase as they recede from the direct rays. Also when the fringes made by the inflexion of one body, and which increase with the distance from the direct rays, are deflected by a second body, the effect of the disposition and of the distances is such as to correct the effect of the first flexion, and the fringes by deflexion of the second body are made to decrease as they recede from the direct rays.

In fig. 15, A P is the pencil inflected by A and forming the first and narrower fringe p; A r is the pencil inflected nearer to A and forming the broader fringe r. Such are the relative breadths, because they are inversely as some power of the distance at which A acts on them. But if B afterwards acts, it is shown by the same reasoning which was applied to the last proposition that r will be less than p; and so in like manner will r' be made less than o', though o' was greater than r', until B's action, and the effects of disposition with the greater proximity of the smaller fringe, altered the proportions.

Proposition VIII.

It is proved by experiment that the inflexion of the second body makes broader fringes or images than its deflexion after the inflexion of the first body; and also that the inflecto-deflexion fringes decrease, and the deflecto-inflexion fringes increase with the distance from the direct rays.

Exp. 1. It must be observed that when we examine the fringes (or images) made by the second edge deflecting the rays which the first had inflected, we can see the effects of the disposition communicated to the rays at a much greater distance of the second edge from the first, than we can perceive the effects of that disposition upon the inflexion by the second edge of the rays deflected by the first. Indeed we only lose the fringes thus made by deflexion, in consequence of their becoming so minute as to be imperceptible to our senses. But it is otherwise with the fringes or images

made by the second edge inflecting the rays which the first had deflected. These can only be seen when the second edge is near the first, because the rays cannot pass on so as to form the images on the chart, if the second is distant from the first. The pencils diverge both by the deflexion and by the inflexion of the first edge. But we can always, when the inflected rays pass too far from the second edge, bring this so near them as to act on them, whereas we in so doing intercept the deflected rays. However, after this is explained, we find no difficulty in examining the effects of the inflexion by the second edge, only we must place it near the first, and thus we have two sets of fringes, one extending into the shadow of the first edge at an inch distance between the two edges; but at three-fourths of an inch, nay, at two inches, or even more, this experiment can well be made.

Exp. 2. At these distances I examined repeatedly the comparative breadths of the two sets. In fig. 16, $a\,b$ is the white disc, on each side of which are fringes; those on the one side, $b\,c$, $c\,d$, are by the inflexion of the second edge; those on the opposite side, $a\,f$, $f\,e$, are by the deflexion of that second edge. I repeatedly measured these sets of fringes, and at various distances from the second edge; and I always found them much broader on the side of the second edge than on the opposite side. Thus $a\,b$ being the breadth of 5, $b\,c$ was 3, and $c\,d$ $4\frac{1}{2}$, while, on the opposite side, $a\,f$ was $=1$ and $f\,e$ only $\frac{3}{4}$ or $\frac{1}{3}$. The fringes by inflexion of the second edge also uniformly increased as they receded from $a\,b$, the direct rays, whereas the opposite fringes as constantly decreased.

Exp. 3. If however the distance between the two edges be reduced, it is observed that the disparity between the two sets of fringes decreases, and they become gradually nearly equal; and when the edges are quite opposite each other there is no difference observable in the two sets. Each ray is disposed and polarized alike and affected alike by the two edges, and no difference can be perceived between the two sets.

Exp. 4. The experiments also agree entirely with the calculus in respect of the relative values of r and v affecting the result. It appears that the fringes by the second edge's inflexion are broader than those by that edge's deflexion, whether we use white or homogeneous light. In the latter, however, the difference is not so considerable. This I have repeatedly tried and made others try, whose sight was better than my own. I may take the liberty of mentioning my friend Lord Douro, who has, I believe, hereditarily, great acuteness of vision.

Proposition IX.

The joint action of two bodies situated similarly with respect to the rays which pass between them so near as to be affected by both bodies, must, whatever be the law of their action, provided it be inversely as some power of the distance, produce fringes or images which increase with the distance from the direct rays.

Let (fig. 17) A and B be the two bodies, and $A\,C=C\,B=a$ be their spheres of

flexion, so that A inflects and B deflects through A C, and A deflects and B inflects through C B. Let C P$=x$, P M$=y$. The force y, exerted by the joint action of A and B on any ray passing between them at P, is equal to $\frac{1}{(a+x)^m}+\frac{1}{(a-x)^n}$, supposing deflexion and inflexion to follow different laws. To find the minimum value of y, take its differential $dy=0$; therefore we have

$$-m(a+x)^{-m-1}dx+n(a-x)^{-n-1}dx=0, \text{ or } m(a-x)^{n+1}=n(a+x)^{m+1}.$$

If $m=n$ (as there is every reason for supposing), then $a-x=a+x$, or $x=0$; and therefore, whatever be the value of m (that is whatever be the law of the force), the minimum value of y is at the point C where A's deflexion begins. The curve S S', which is the locus of M, comes nearest the axis at C, and recedes from that axis constantly between C and B. Hence it is plain that the fringes must increase (they being in proportion to the united action of A and B) from C to B; and in like manner must those made by B's deflexion and A's inflexion increase constantly from C to A; and this is true whatever be the law of the bending force, provided it is in some inverse ratio to the distance.

Proposition X.

It is proved by experiment that the fringes or images increase as the distance increases from the direct rays.

Exp. 1. Repeated observations and measurements satisfy us of this fact. We may either receive the images on a chart at various distances from the double edge instrument, approaching the edges until the fringes appear, or we may receive them on a plate of ground glass held between the sun and the eye. We may thus measure them with a micrometer; but no such nicety is required, because their increase in breadth is manifest. The only doubt is with respect to their relative breadth when the edges are not very near and just when they begin to form fringes. Sometimes it should seem that these very narrow fringes decrease instead of increasing. However, it is not probable that this should be found true, at least when care is taken to place the two edges exactly opposite each other; because if it were true that at this greater distance of A from B (fig. 17) they decreased, then there must be a minimum value of P M between C and B, and between C and A; and consequently the law of flexion must vary in the different distances of A and B from the rays P, a supposition at variance it should seem with the law of continuity.

Exp. 2. The truth of this proposition is rendered more apparent by exposing the two edges to the rays forming the prismatic spectrum. The increase is thus rendered manifest. If the fringes are received on a ground glass plate, you can perceive twelve or thirteen on each side of the image by the direct rays. It is also worth while to make similar observations on artificial lights, and on the moon's light. The proposition receives additional support from these. But care must always be taken in such observations, which require the eye to be placed near the edges, that we are

not misled by the effect of the small aperture in reversing the action of the edges. Thus when viewing the moon or a candle through the interval of two edges, one being in advance of the other, we have the coloured images (or fringes) cast on the wrong side. But if we are only making the experiment required to illustrate this proposition, the edges being to be kept directly opposite, no confusion can arise.

It is to be noted that the increase of breadth in the fringes is not very rapid in any of these experiments; nor are we led by the calculus to expect it. Thus suppose $m=1$, we find $\left(\text{because } y=\frac{2a}{a^2-x^2}\right)$ at the point C, when $x=0$, the breadth should be proportional to $\frac{2}{a}$. Take $x=\frac{a}{10}$, and the breadth is as $\frac{200}{99}$, or the breadth of the one fringe is to the other only as 200 to 198 or 100 : 99. We need not wonder therefore if there is only a gradual increase of breadth from C to B and from C to A. The increase is more rapid between $x=\frac{a}{2}$ and B than between C and $\frac{a}{2}$. Thus between the value of $x=\frac{a}{4}$ and $\frac{a}{2}$ the increase is as 4 : 5. But from $\frac{a}{2}$ to $\frac{3a}{4}$ the increase is as 7 : 12; and this too agrees exactly with the experiments; for as the edges are approached the increase of the fringes becomes more apparent.

Proposition XI.

The phenomena described in the foregoing propositions are wholly unconnected with interference, and incapable of being referred to it.

1. When the fringes in the shadow are formed by what is supposed to be interference, there are also formed other fringes outside the shadow and in the white light. If the rays passing on one side the bending body (as a pin or needle) are stopped, the internal fringes on the opposite side of the shadow are no longer seen. But no effect whatever is produced on the external fringes. These continue as long as the rays passing on the same side of the body on which they are formed, continue to pass. The external fringes have many other properties which wholly distinguish them from the internal or interference fringes.

2. Interference is said to be in proportion to the different lengths of the interfering rays, and not to operate unless those lengths are somewhat near an equality. In my experiments the second body may be placed a foot and a half away from the first, and the fringes by disposition are still found, though much narrower than when the bending bodies are more near to one another.

3. The breadth of the interference fringes is said to be in some inverse proportion to the difference in length of the interfering rays. It is commonly said to be inversely as that difference.

In fig. 20, A is the first and B the second edge. By interference the fringe at C should be broadest and at D narrowest, because $AC-BC=AO$ is less than $AD-BD=AP$; and so as you recede from D, the fringes should become broader and broader, because the two rays become more nearly equal. But the very reverse is

notoriously the case, the breadth of the fringes decreasing with their distance from the direct rays.

4. In the case of the fringes formed by the second body inflecting and the first deflecting, there can be no interference at all; for the whole action is on one and the same pencil or beam. A deflects and then B inflects the same ray; and when a third edge is placed on the opposite side to B, it only deflects the same ray, which is thus twice bent further from the direct rays, the last bending increasing that distance.

5. Let A be the first and B the second edge as before (fig. 20). Suppose B to be moveable, and find the equation to the disposing force at different distances of the two edges, we shall find this to be $y=\frac{1}{\sqrt{a^2+b^2}-\sqrt{(a-x)^2+b^2}}$, a being $=$AE, $b=$ED, and AB$=x$. But all the experiments show it to be $y=\frac{a}{x^2}$, a wholly different curve.

Again, let B be fixed, or the distance of the two edges be constant, we shall get the equation (a being $=$AE, $b=$BE, $b=$DE and EC$=x$) $y=\frac{1}{\sqrt{a^2+(x-b)^2}-\sqrt{c^2+x^2}}$, also a wholly different curve from the conic hyperbola, which all experiments give. Therefore the conclusion from the whole is that the phenomena have no reference to interference.

Having delivered the doctrines resulting from these experiments, I have some few particulars to add, both as illustrating and confirming the foregoing propositions, as removing one or two difficulties which have occurred to others until they were met by facts, and also as showing the tendency of the results at which we have arrived.

1. It may have been observed that in all these propositions I have taken for granted the inflexion of the rays by the body first acting upon them as well as their deflexion by that body, and have reasoned on that supposition. It is, however, not to be denied that we cannot easily perceive the fringes made by the single inflexion, as we can without any difficulty perceive those made by the single deflexion, and fully described in Proposition I. Sir I. Newton even assumes that no fringes are made within the shadow. I here purposely keep out of view the fringes made in the shadow of a hair or other small body, because the principle of interference there comes into play. However, I will now state the grounds of my assuming inflexion and separation of the rays by their different flexibility, when only a single body acts on them. In the *first* place, the first body does act in some way; for the second only acts after the first, and if the first be removed the fringes made in its shadow by the second at once vanish. *Secondly*, these fringes made by the second depend upon its proximity to the first. *Thirdly*, the following experiment seems decisive. Place instead of a straight edge one of the form in fig. 18, and then apply at some distance from it, the second edge, as in the former experiments. You find that the fringes assume the form, somewhat like a small tooth-comb, of $a\,b$. If the second edge is

furnished with a similar curve surface the form is more complete, as in *c d*. But the straight edge being used after the first flexion of the curved one, clearly shows that the first edge bends as well as the second, indeed more than the second, for the side of the figure answering to that curved edge is most curved. *Fourthly*, the whole experiments with two edges directly opposite each other negative the idea of there being no inflexion; indeed they seem to prove the inflexion equal to the deflexion. The phenomena under Proposition X. can in no way be reconciled to the supposition of the first edge not inflecting the rays*.

2. We must ever keep in view the difference between the fringes or images described by Sir I. Newton and measured by him, as made by the rays passing on each side of a hair, and the fringes or images which are made without the interference of rays passing on both sides. It is clear that the rays which form those fringes with their dark intervals do not proceed after passing the hair in straight lines. Sir I. Newton's measures† prove this; for at half a foot from the hair he found the first fringe $\frac{1}{170}$th of an inch broad, and the second fringe $\frac{1}{300}$; and at nine feet distance the former were $\frac{1}{33}$, the latter $\frac{1}{58}$, instead of being $\frac{1}{8}$ and $\frac{1}{10}$, and the latter less than $\frac{1}{16}$, and so of all the other measures in the table, each being invariably about one-third what it ought to be if the rays moved in straight lines; and this also explains why the fringes do not run into one another, or encroach on the dark intervals in the case of the hair, as they must do if the rays moved in straight lines.

But the case of the fringes or images which we have been examining and reasoning upon is wholly different. I have measured the breadths of those formed by disposition and polarization, and found that they are broad in proportion to the distance from the bending edge of the chart on which they are received; and vary from the results given by similar triangles in so trifling a degree, that it can arise only from error in measurement. Thus in an average of five trials, at the relative distances of 41 and 73 inches, the disc was $6\frac{3}{8}$ at the shorter, and $10\frac{1}{8}$ at the longer distance; the fringe next it $3\frac{7}{10}$ at the shorter, and $5\frac{7}{10}$ at the longer distance, whereas the proportions by similar triangles would have been $9\frac{1}{8}$ and $5\frac{1}{8}$, so that the difference is small, and is by excess, and not, as in the hair experiment, by defect. Had the difference been as in Sir I. Newton's experiment, instead of $10\frac{1}{8}$ and $5\frac{7}{10}$, it would have been $3\frac{1}{34}$ and $1\frac{7}{34}$. In another measurement at 101 and 158 inches respectively, the disc was $15\frac{1}{8}$, the fringe $8\frac{1}{8}$ instead of $14\frac{3}{8}$ and $9\frac{1}{8}$ respectively. But by Sir I. Newton's proportions these should have been $4\frac{3}{8}$ and $3\frac{1}{34}$. It is plain that if the measures had been taken with the micrometer instruments, which had not been then furnished, there would have been no deviation. I have since tried the experiment, not as above, on the fringes formed by the double-edged instrument, but on those formed by one edge at a distance behind the other, and have found no reason to doubt that the rays follow a rectilinear course.

* If you hold a body between the eye and a light, as that of a candle, and approach it to the rays, you see the flame drawn towards the body; and a beginning of images or fringes is perceived on that side.

† Optics, B. iii. obs. 3.

It may further be observed, that in the fringes or images by disposition and polarization, the dark intervals disappear at short distances from the point of flexion, and that the fringes run into one another, so that we find the red mixed with the blue and violet. This is one reason why I often experimented with the prismatic rays.

3. It follows from the property of light, which I have termed disposition, on one side the ray, and polarization on the opposite side, superinduced by flexion, that those two sides only being affected, the other two at right angles to these are not at all affected by the flexion which has disposed and polarized the two former. Consequently, although an edge placed parallel to the disposing edge and opposite to it acts powerfully on the disposed light, yet an edge placed at right angles to the former edge or across the rays, does not affect them any more than it would rays which had not been subjected to the previous action of a first edge. Thus (fig. 19) if *a b c d* be the section of the ray, an edge parallel to *a b*, after the ray has been disposed, will affect the ray greatly, provided it had been disposed by an edge also parallel to *a b*. The sides *a b* and *c d*, however, are alone affected; and therefore the second edge, if placed parallel to *a d* or *b c*, will not at all bend the ray more or make images (or fringes) more powerfully than it would do if no previous flexion and disposition had taken place. Let us see how this is in fact: *e f g h* is the distended disc after flexion, by passing through the aperture of the two-edged instrument (Plate XI.). It is slightly tinged with red at the two ends *f g* and *e h*, beyond which, and in the shadow of the edges, are the usual fringes or coloured images by flexion and disposition, *e*, *c*, the edges being parallel to *e h*, *f g*. Place another edge at some distance from the two, as 3 or 4 inches, and parallel to these two, but in the light, and you will see in the disc a succession of narrow fringes parallel to the edges, and in front of the third edge's shadow. These fringes are on the white disc, and their colours are very bright, much more so than the colours of those fringes described in Proposition I., and which are fringes made by deflexion without any disposition. But whether this superior brightness is owing to the glare of the disc's light being diminished by the flexion of the first two edges, or not, for the present I stop not to inquire. This is certain, that if the third edge be placed across the beam, and at right angles to the two first edges, you no longer have the small fringes. They are not formed in the direction *h g*, parallel to the edges as now placed. If the double edges are changed, and are placed in the direction *h' g'*, you again have the bright fringes; but then, if the third edge is now placed parallel to *h' e'*, you cease to have them. Care must, however, be taken in this experiment not to mistake for these bright fringes the ordinary deflexion fringes made by one flexion without disposition, as described in Proposition I. For these may be perceived, and even somewhat more distinctly in the disc than in the full light of the white pencil or beam.

Now are these bright fringes only the flexion fringes, that is fringes by simple flexion without disposition? To ascertain this I made these experiments.

Exp. 1. If they are the common fringes, and only enlarged by the greater divergence of the rays after flexion, and more bright by the dimness of the distended disc,

then it will follow that the greater the distension, and the greater the divergence of the rays, the broader will be the bright fringes in question. I repeatedly have tried the thing by this test, and I uniformly find that increasing the divergence, by approaching the edges of the instrument, has no effect whatever in increasing the breadth of the fringes in question.

Exp. 2. If these fringes are not connected with disposition, it will follow that the distance of the edge which forms them from the double-edged instrument cannot affect them. But I have distinctly ascertained that their breadth does depend on that distance, and in order to remove all doubt as to the distance between the chart and the third edge which forms them, I allowed that edge to remain fixed, and varied its distance from the other two by bringing the double-edge instrument nearer the third edge. The breadths of the bright fringes varied most remarkably, being in some inverse power of that distance. Thus, to take one measurement as an example of the rest, at 4 feet from the third edge the chart was fixed and the third edge kept constantly at that distance from it. Then the double-edge instrument was placed successively at $14\frac{1}{2}$, at 9 and at $4\frac{1}{2}$ eighths of an inch from the third edge. The breadths were respectively 2, $3\frac{3}{4}$ and $4\frac{1}{2}$ twentieths of an inch. In some experiments these measures approached more nearly the hyperbolic values of y, but I give the experiment now only for the important and indeed decisive evidence which it affords, that these fringes are caused by disposition, and are wholly different from those formed without previous flexion.

Exp. 3. If the greater breadth of these fringes is owing to dispersion, then they should be formed more in the rays of the prismatic spectrum than in white light, or even in light bent by flexion. Yet we find it more difficult to trace fringes across the prismatic spectrum than in white light, and more difficult across the spectrum when there is divergence, than when formed parallel to its sides when there is no divergence. There are fringes formed, but of the narrow kind, which are described in Prop. I.

Exp. 4. I have tried the effect on the fringes in question of the curvilinear edge described in the first article of these observations, and the effect of which is represented in fig. 18. It is certain that at a distance from the double-edge instrument the third edge seems only to form fringes rectilinear, or of its own form. But when placed very near, as half an inch from the instrument, plainly there is a curvilinear form given to the fringes in question; and this is most easily perceived, when, by moving the third edge towards the side of the pencil, you form the smaller fringes so as to be drawn across or along the greater ones made by the two first edges.

I think, without pursuing this subject further, it must be admitted that these fringes in light, which is bent and disposed, lend an important confirmation to the doctrine of disposition. It is clear that the rays are affected only on two of their four sides, or $a\,b$ and $c\,d$, if these are parallel to the bending body's edge, and not at all on the sides $c\,b$ and $d\,a$; that, on the other hand, $c\,b$ and $d\,a$ are affected when the

edges are placed parallel to these two sides of the rays; and thus the connection of the fringes in question, with the preceding action of which disposed and polarized, is clearly proved.

4. It is an obvious extension and variation of this experiment both to apply edges parallel to the first and disposing edges, and also to apply edges at right angles to their direction; and important results follow from this experiment. But until a more minute examination of the phenomena with accurate admeasurements can be had, I prefer not entering on this subject further than to say, that the extreme difficulty of obtaining fringes or images at once from the edges parallel to the first two, and from edges at right angles to these, indicates an action not always at right angles to the bending body, but whether conical or not I have not hitherto been able to ascertain. That the first body only disposes and polarizes in one direction is certain. But it seems difficult to explain the effect of the first two edges in preventing the fringes or images from being made by the second at right angles to those formed by the first two edges, if no lateral action exists. One can suppose the approaching of those two first edges to make the fringes narrower and narrower than those which the second two edges form when placed at right angles to the first. But this is by no means all that happens. There is hardly any set of fringes at all formed at right angles to the first set (parallel to the first two edges) when the first two are approached so near each other as greatly to distend the disc.

5. I reserve for future inquiry also the opinion held by Sir I. Newton, that the different homogeneous rays are acted upon by bodies at different distances, this action extending furthest over the least refrangible rays. He inferred this from the greater breadth of the fringes in those rays.

It is in my apprehension, though I once held a different opinion*, not impossible to account for the difference of the breadth of the fringes by the different flexibility of the rays; and the reasoning in one of the foregoing propositions shows how this inquiry may be conducted. But one thing is certain, and probably Sir I. Newton had made the experiment and grounded his opinion upon the result. If you place a screen, with a narrow slit in the prismatic spectrum's rays, parallel to the rectilinear sides, and then place a second prism at right angles to the first and between the screen and the chart, you will see the image of the slit drawn on one side, the violet being furthest drawn, the red least drawn; but you will find no difference in the breadth of the image cast by the slit. Flexion, however, operates in a different manner, because it acts on rays, which, though of the same flexibility, are at different distances from the body.

6. The internal fringes in the shadow (said by interference) deserve to be examined much more minutely than they ever have been; and I have made many experiments on these, by which an action of the rays on one another is, I think, sufficiently proved. I shall here content myself with only stating such results as bear on

* Philosophical Transactions, 1797.

the question of interference affecting my own other experiments. *First.* I observe that when one side of a needle or pin is grooved so as to be partly curvilinear, the other side remaining straight, we have internal fringes of the form in fig. 21. *Secondly.* It is not at all necessary the pin or other body forming them should be of very small diameter, although it is certain that the breadth of the fringes is inversely as the diameter. I have obtained them easily from a body one-quarter or one-third of an inch in diameter, but they must be received at a considerable distance from the body. *Thirdly,* and this is very material as to interference at all affecting my experiments, although certainly the internal fringes vanish when the rays are stopped coming from the opposite side of the object, the external fringes are not in the smallest degree affected, unless you stop the light coming on their own side; stopping the opposite rays has no effect whatever. Thus, stopping the light on the side *a* (fig. 19), the fringes *f f* vanish, but not the external fringes *c*. This at once proves there is no interference in forming the external ones. *Lastly.* I may observe, that the law of disposition and polarization in some sort, though with modification, affects the internal fringes as well as the external.

It is a curious fact connected with polarization by inflexion, and which indeed is only to be accounted for by that affection of light, that nothing else prevents the rays from circulating round bodies exposed to them, at least bodies of moderate diameter. If the successive particles of the surface inflected, one particle acting after the other, the rays must necessarily come round to the very point of the first flexion. We should thus see a candle placed at A (fig. 22) when the eye was placed at B, because the rays would be inflected all round; and even in parts of the earth where the sea is smooth, nothing but the small curvature of the surface could prevent us from seeing the sun many hours after light had begun by placing the eye close to the ground. This, however, in bodies of a small diameter, must inevitably happen. The polarization of the rays alone prevents it, by making it impossible they should be more than once inflected on their side which was next the bending body, therefore they go on straight to C. But for polarity they must move round the body.

7. It must not be lightly supposed, that because such inquiries as we have been engaged in are on phenomena of a minute description and relate to very small distances, therefore they are unimportant. Their results lead to the constitution of light, and its motion, and its action, and the relations between light and all bodies. I purposely abstain from pursuing the principles which I have ventured to explain into their consequences, and reserve for another occasion some more general inquiries founded upon what goes before. This course is dictated by the manifest expediency of first expounding the fundamental principles, and I therefore begin by respectfully submitting these to the consideration of the learned in such matters.

In the meantime, however, I will mention one inference to be drawn from the foregoing propositions of some interest.

As it is clear that the disposition varies with the distance, and is inversely as that

distance, and as this forms an inherent and essential property of the light itself, what is the result? Plainly this, that the motion of light is quite uniform after flexion, and apparently before also. The flexion produces acceleration but only for an instant. If ss is the space through which the ray moves after entering the sphere of flexion, and v the velocity before it enters that sphere; it moves after entering with a velocity $=\sqrt{v^2+Zdz}$, Z being the law of the bending force. Then this is greater than v; consequently there is an acceleration, though not very great; but because $y=\frac{a}{x}$, if s is the space, t the time, the force of acceleration is $\frac{s}{tds}\times\frac{tds-sdt}{t^2}$; but $y=\frac{a}{x}$ shows that s is as t, else $y=\frac{a}{x}$ would be impossible; therefore the accelerating force $\frac{s}{ds}\times\frac{tds-sdt}{t^2}=0$, and so it is shown there is no acceleration after the ray leaves the sphere of flexion.

Description of the Instruments.

PLATE XII.

Is the instrument with two plates or edges. A, B, horizontal, D, C vertical; the former moved by the screw E, which has also a micrometer for the distances on the scale G; the latter, in like manner, moved by F, connected with micrometer and scale H.

PLATE XIII.

Is the instrument with four surfaces. A D, a d are two parallel plates, moving horizontally by a rack and pinion E. Each plate has an edge composed of four surfaces; A, a, a sharp edge or very narrow surface; B, b, a flat surface; C, c, a cylindrical surface of large radius of curvature, and so flat; D, d, one of small radius, and so very convex: this is represented on the figure by A` B` C` D` beside the other. Care is to be taken that A B C D and a b c d be a perfectly straight line, made up of the sharp edge, the plane surface and the tangents to the two cylinders. H is a plate with a sharp and straight edge, o p, which can be brought by its handle F to come opposite to the compound edge a b c d, when it is desired to try the flexion by the latter, without another flexion by an opposite compound edge, but only with a flexion by a rectilinear simple edge.

PLATE XIV.

Is the instrument by which is tried the *experimentum crucis* on the action of the third edge, and also the experiments on the distances of the edges as affecting the disposing force. G is the groove in which the uprights H, I, K move. There is a scale

graduated, F, by which the relative distances can always be determined of the plates A, C and B. A moves up and down upon H, B upon I, and C upon K; each plate is moved up and down by rack and pinion D. The uprights also move along the groove G by rack and pinion E.

PLATE XV.

Is the instrument for ascertaining more nicely the effects of distance on disposition. A is a plate with graduated edge; it moves vertically on a pivot, and its angle with the horizontal line is measured by the quadrant E. A also moves horizontally, and its horizontal angle is measured by the quadrant K. B is another plate with graduated edge, moving in a groove D, by rack and pinion H, and along a graduated beam I. F is a fine micrometer, by which the distance of A above B, when A is horizontal, can always be measured to the greatest nicety by the circle F and the scale G.

PLATE XVI.

Is an instrument also for measuring the effect of the distance of the edges upon the disposing forces. C C C is a graduated beam, adjusted by the spirit-level, and on it moves the upright on which a plate A moves by micrometer screw E, so that the distance of A from the rays that pass along C C C after flexion by a plate fixed at one end of the beam, can be ascertained by the scale D. I have experimented with this, but I did not find it so easy to work by as the other apparatus. C C C is brought to an exact level by screws not noted in the drawing.

XIII. *General Methods in Analysis for the resolution of Linear Equations in Finite Differences and Linear Differential Equations.*

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Preliminary Remarks.

1. THE investigations presented in this paper consist of two parts; the first offers a solution, in a certain qualified sense, of the general linear equation in finite differences; and the second will be found to give an almost complete analysis of the resolution in series of the general linear differential equation with rational factors. The second part is deduced directly from the results of the first, although the subjects of which they respectively treat appear to be wholly independent of each other.

With the exception of a few cases capable of solution by partial and artificial methods, there does not at present exist any mode of solving linear equations in finite differences of an order higher than the first; and with reference to such equations of the first order, we are obliged to be content with those insufficient forms of functions which are intelligible only when the independent variable is an integer, and which may be obtained directly from the equation itself by merely giving to the independent variable its successive integer values. It is in this insufficient and qualified sense that the solutions here given are to be taken; and the first part of the following investigations may be considered as an extension of this form of solution from the general equation of the first order to the general equation of the nth order.

Linear Equations in Finite Differences.

2. A complete analytical theory of the general equation of the nth order,

$$u_x = P_x u_{x-1} + Q_x u_{x-2} + R_x u_{x-3} + S_x u_{x-4} + \ldots + W_x u_{x-n+1} + Z_x u_{x-n} + G_x, \quad \ldots \quad (1.)$$

would involve its resolution into a series of equations of the first order of the form

$$u_x - P'_x u_{x-1} = G'_x,$$
$$u_x - P''_x u_{x-1} = G''_x,$$
$$\ldots \quad \ldots \quad \ldots$$
$$u_x - P^{(n)}_x u_{x-1} = G^{(n)}_x;$$

from which the complete solution would result, so far as known methods extend, in the form

$$u_x = P_1 P_2 .. P_x \Sigma\left(\frac{G'_x}{P'_1 P'_2 .. P'_{x+1}}\right) + ... + P^{(n)}_1 P^{(n)}_2 .. P^{(n)}_x \Sigma\left(\frac{G^{(n)}_x}{P^{(n)}_1 P^{(n)}_2 .. P^{(n)}_{x+1}}\right),$$

or in an expanded form,

$$\begin{aligned}
u_x = {} & G'_x + P'_x G'_{x-1} + P_{x-1} P'_x G'_{x-2} + P'_{x-2} P_{x-1} P'_x G'_{x-3} + ... + c' P'_m P_{m+1} ... P'_x \\
& + G''_x + P''_x G''_{x-1} + P''_{x-1} P''_x G''_{x-2} + P''_{x-2} P''_{x-1} P''_x G''_{x-3} + ... + c'' P''_m P''_{m+1} ... P''_x \\
& + . \quad . \quad . \quad . \quad . \\
& + . \quad . \quad . \quad . \quad . \\
& + G^{(n)}_x + P^{(n)}_x G^{(n)}_{x-1} + P^{(n)}_{x-1} P^{(n)}_x G^{(n)}_{x-2} + P^{(n)}_{x-2} P^{(n)}_{x-1} P^{(n)}_x G^{(n)}_{x-3} + ... + c^{(n)} P^{(n)}_m P^{(n)}_{m+1} ... P^{(n)}_x .
\end{aligned}$$

The last column contains, as is well known, the general solution of the original equation deprived of the term G_x; and the remaining columns contain the particular solution of the original equation.

3. The investigation the results of which are given in this part, although it actually succeeds in solving the original equation, will be found to contribute little or nothing to the analytical theory as above explained; and this arises from the circumstance, that the particular solution, instead of being produced in the separated form above written, is produced in an aggregated form,

$$G_x + AG_{x-1} + BG_{x-2} + \ldots ;$$

and the complementary part of the general solution, instead of being produced as above, appears in the form of a *sum* of the complementary functions above written, the constants c', c'', &c. being the same in all. But as we shall thus obtain a solution with an arbitrary constant, capable of solving the original equation deprived of G_x, we have it in our power to solve the equation completely by reducing the order of the equation in successive steps.

If we take the equation of the first order,

$$u_x = P_x u_{x-1} + G_x,$$

and arrive at its solution, not properly by any analytical method, but by giving to x the successive values

$$x,\ x-1,\ x-2 \ldots .. m+1,\ m,\ m-1,$$

and eliminating all values of u_x between the first and the last, we have

$$\begin{aligned}
u_x &= P_x u_{x-1} + G_x \\
&= P_x (P_{x-1} u_{x-2} + G_{x-1}) + G_x \text{ or } P_x P_{x-1} u_{x-2} + P_x G_{x-1} + G_x \\
&= P_x P_{x-1} (P_{x-2} u_{x-3} + G_{x-2}) + P_x G_{x-1} + G_x \text{ or } P_x P_{x-1} P_{x-2} u_{x-3} + P_x P_{x-1} G_{x-2} + P_x G_{x-1} + G_x \\
&= \ldots . \qquad\qquad \ldots . \\
&= (P_x P_{x-1} \ldots P_m) u_{m-1} + (P_x .. P_{m+1}) G_m + (P_x .. P_{m+2}) G_{m+1} + \ldots + P_x P_{x-1} G_{x-2} + P_x G_{x-1} + G_x
\end{aligned}$$

$$=(P_x\ldots P_m)\left\{u_{m-1}+\frac{G_m}{P_m}+\frac{G_{m+1}}{P_mP_{m+1}}+\ldots.+\frac{G_{x-2}}{P_m\ldots P_{x-2}}+\frac{G_{x-1}}{P_m\ldots P_{x-1}}+\frac{G_x}{P_m\ldots P_x}\right\}$$

$$=P_x\ldots P_m\left(\Sigma\frac{G_{x+1}}{P_m\ldots P_{x+1}}+c\right);$$

which is the solution ordinarily given, though it is arrived at by a process somewhat less coarse than the above.

By applying the same process of successive elimination to the general linear equation (1.), and carefully observing the law by which the entrance of the factors P_x, Q_x, R_x, &c. is governed, it will be found that an exactly similar solution may be found in the form

$$u_x=v^x\left\{P_x\ldots P_m\left(\Sigma\left(\frac{G_{x+1}}{P_m\ldots P_{x+1}}\right)+c\right)\right\},$$

or

$$u_x=G_x+P_xG_{x-1}+v^x(P_xP_{x-1}).G_{x-2}+v^x(P_x\ldots P_{x-3}).G_{x-3}+\ldots+v^x(P_x\ldots P_{m+1}).G_m+cv^x(P_x\ldots P_m);$$

where v denotes the sum of a set of distributive operations V_1, V_2, V_3, ... V_{n-1} not of a strictly algebraical character, which are capable of being performed only upon factorial expressions containing consecutive values of P_x, and which have the following significations. V_1 denotes one operation of this character, signifying that the factor $P_{x-1}P_x$ is changed into Q_x as often as it occurs, any term in which it does not occur disappearing, and the sum of the terms thus obtained being the result of the operation; so that, for example,

$$V_1(P_{x-1}P_x)=Q_x,\ V_1^2(P_{x-1}P_x)=0,$$

$$V_1(P_{x-2}P_{x-1}P_x)=Q_{x-1}P_x+P_{x-2}Q_x,\ V_1^2(P_{x-2}P_{x-1}P_x)=0,$$

$$V_1(P_{x-3}P_{x-2}P_{x-1}P_x)=Q_{x-2}P_{x-1}P_x+P_{x-3}Q_{x-1}P_x+P_{x-3}P_{x-2}Q_x,\ V_1^2(P_{x-3}P_{x-2}P_{x-1}P_x)=2Q_{x-2}Q_x,$$

&c. &c.

Again, V_2 denotes another operation of a similar character, signifying that the factor $P_{m-2}P_{m-1}P_m$ is changed into R_m as often as it occurs, the result of the operation being as before the sum of the terms; so that, for example, we have

$$V_2(P_{x-2}P_{x-1}P_x)=R_x,$$

$$V_2(P_{x-3}P_{x-2}P_{x-1}P_x)=R_{x-1}P_x+P_{x-3}R_x,$$

$$V_2(P_{x-4}P_{x-3}P_{x-2}P_{x-1}P_x)=R_{x-2}P_{x-1}P_x+P_{x-4}R_{x-1}P_x+P_{x-4}P_{x-3}R_x,$$

$$V_2(P_{x-4}\ldots P_x)=R_{x-3}P_{x-2}P_{x-1}P_x+P_{x-4}R_{x-3}P_{x-1}P_x+P_{x-4}P_{x-4}R_{x-1}P_x+P_{x-4}P_{x-4}P_{x-3}R_x,$$

$$V_2^2(P_{x-5}\ldots P_x)=2R_{x-3}R_x,\ \&c.\ \&c.;$$

V_3 denotes the change in a similar manner of $P_{m-3}P_{m-2}P_{m-1}P_m$ into S_m;

. . .

. . .

V_{n-2} denotes the change in a similar manner of $P_{m-n+2}\ldots P_m$ into W_m;

and

V_{n-1} denotes the change in a similar manner of $P_{m-n+1}\ldots P_m$ into Z_m.

It might at first sight be supposed that this process, if successful at all, would give the complete complementary solution in the form

$$u_x = c_1 s^x(P_1..P_x) + c_2 s^x(P_2..P_x) + ..;$$

but it will be found that in reality this introduces only one arbitrary constant.

It now remains to place these expressions under a properly algebraic form, and to verify the result; and in order to do this we must express the general term $s^x(P_x...P_{x+1})$ in terms of the factors of the original equation; and afterwards give to p, which in the first instance is regarded as a constant, the successive values required for forming the several terms of the solution.

This may be done as follows:—

Let $\frac{Q_x}{P_{x-1}P_x} = q_x$, $\frac{R_x}{P_{x-2}P_{x-1}P_x} = r_x$, $\frac{S_x}{P_{x-3}P_{x-2}P_{x-1}P_x} = s_x$, ... $\frac{W_x}{P_{x-n+2}...P_x} = w_x$, and $\frac{Z_x}{P_{x-n+1}...P_x} = z_x$.

Then it is easily seen that

$$V_1(P_x...P_{p+1}) = P_x...P_{p+1}\{q_{p+2} + q_{p+3} + ... + q_x\} = P_x...P_{p+1}\Sigma_{p+1}^x q_{x+1},$$

$$V_2(P_x...P_{p+1}) = P_x...P_{p+1}\{r_{p+3} + r_{p+4} + ... + r_x\} = P_x...P_{p+1}\Sigma_{p+2}^x r_{x+1},$$

and generally

$$v(P_x...P_{p+1}) = P_x...P_{p+1}\{\Sigma_{p+1}^x q_{x+1} + \Sigma_{p+2}^x r_{x+1} + \Sigma_{p+3}^x s_{x+1} + ... + \Sigma_{p+n-2}^x w_{x+1} + \Sigma_{p+n-1}^x z_{x+1}\}.$$

To find $V_1^3(P_x..P_{p+1})$, it will be convenient to proceed by steps, beginning with a small number of terms.

Thus

$$V_1(P_x...P_{x-3}) = (P_x...P_{x-3})(q_x + q_{x-1} + q_{x-2}),\ \frac{1}{2}V_1^2(P_x...P_{x-3}) = P_x...P_{x-3}(q_x q_{x-2})$$

$$V_1(P_x...P_{x-4}) = (P_x...P_{x-4})(q_x + q_{x-1} + q_{x-2} + q_{x-3}),\ \frac{1}{2}V_1^2(P_x...P_{x-4}) = P_x...P_{x-4}\big(q_x(q_{x-2} + q_{x-3}) + q_{x-1}q_{x-3}\big)$$

$$V_1(P_x...P_{x-5}) = (P_x...P_{x-5})(q_x + q_{x-1} + q_{x-2} + q_{x-3} + q_{x-4}),$$

$$\frac{1}{2}V_1^2(P_x...P_{x-5}) = (P_x...P_{x-5})\big(q_x(q_{x-3} + q_{x-3} + q_{x-4}) + q_{x-1}(q_{x-3} + q_{x-4}) + q_{x-2}q_{x-4}\big)\ \&c.;$$

and generally, $V_1(P_x...P_{p+1})$ being $P_x...P_{p+1}(\Sigma_{p+1}^x q_{x+1})$, we have

$$\frac{1}{2}V_1^2(P_x...P_{p+1}) = P_x...P_{p+1}(q_x\Sigma_{p+1}^{x-2}q_{x+1} + q_{x-1}\Sigma_{p+1}^{x-3}q_{x+1} + .. + q_{p+1}\Sigma_{p+1}^{p+2}q_{x+1})$$

$$= P_x...P_{p+1}\Sigma_{p+2}^x(q_{x+1}\Sigma_{p+1}^{x-1}q_{x+1}).$$

Similarly, it will be seen that

$$\frac{1}{2.3}V_1^3(P_x...P_{p+1}) = P_x...P_{p+1}\Sigma_{p+3}^x\big(q_{x+1}\Sigma_{p+3}^{x-1}(q_{x+1}\Sigma_{p+1}^{x-1}q_{x+1})\big),\ \text{and so on.}$$

In like manner we shall find

$$\frac{1}{2}V_2^2(P_x...P_{p+1}) = P_x...P_{p+1}\Sigma_{p+3}^x(r_{x+1}\Sigma_{p+2}^{x-2}r_{x+1})$$

$$\frac{1}{2.3}V_3^3(P_x...P_{p+1})=P_x...P_{p+1}\Sigma_{p+3}^x\left(r_{x+1}\Sigma_{p+3}^{x-3}(r_{x+1}\Sigma_{p+2}^{x-3}r_{x+1})\right), \text{ and so on,}$$

$$\frac{1}{2}V_m^3(P_x..P_{p+1})=(P_x..P_{p+1})\Sigma_{p+2m+1}^x(v_{x+1}\Sigma_{p+m}^{x-m}v_{x+1}),$$

$$\frac{1}{2.3}V_m^3(P_x..P_{p+1})=(P_x..P_{p+1})\Sigma_{p+2m+3}^x(v_{x+1}\Sigma_{p+2m+1}^{x-m}(v_{x+1}\Sigma_{p+m}^{x-m}v_{x+1})), \text{ and so on,}$$

v_x being that term of the series $q_x r_x s_x$, &c. which corresponds to the operation V_m, as q_x corresponds to V_1, r_x to V_2, &c.

$$V_1V_3(P_x...P_{p+1})=P_x...P_{p+1}\Sigma_{p+4}^x(r_{x+1}\Sigma_{p+3}^{x-3}q_{x+1}),$$

$$V_lV_m(P_x...P_{p+1})=P_x...P_{p+1}\Sigma_{p+m+l+1}^x(t_{x+1}\Sigma_{p+m}^{x-l}v_{x+1}), \ (t_x \text{ corresponding to } V_l),$$

$$V_l^2V_m(P_x...P_{p+1})=P_x...P_{p+1}\Sigma_{p+m+2l+3}^x\left(t_{x+1}\Sigma_{p+m+l+1}^{x-l}(t_{x+1}\Sigma_{p+m}^{x-l}v_{x+1})\right), \text{ &c. &c.}$$

Finally, if $N'_{x,p}+N''_{x,p}+N'''_{x,p}+..$ represent a series in which

$$N'_{x,p}=1,\ N''_{x,p}=\Sigma_{p+1}^x q_{x+1}+\Sigma_{p+2}^x r_{x+1}+..+\Sigma_{p+x-1}^x z_{x+1},$$

and generally

$$N_{x,p}^{(a+1)}=\Sigma_{p+2a-1}^x(q_{x+1}N_{x-1,p}^{(a)})+\Sigma_{p+3a-1}^x(r_{x+1}N_{x-2,p}^{(a)})+\Sigma_{p+4a-1}^x(s_{x+1}N_{x-3,p}^{(a)})+....$$
$$+\Sigma_{p+(n-1)a-1}^x(w_{x+1}N_{x-n+2,p}^{(a)})+\Sigma_{p+na-1}^x(z_{x+1}N_{x-n+1,p});$$

then, if this series be called $N_{x,p}$, we shall find that $\epsilon^a(P_x...P_{p+1})=(P_x...P_{p+1})N_{x,p}$.

It may be here observed that the number of the terms of the series $N'_{x,p}+N''_{x,p}+..$ cannot exceed $\frac{1}{2}(x-p)+1$ when $x-p$ is even, and $\frac{1}{2}(x-p+1)$ when $x-p$ is odd; and since p has the successive values $x-2$, $x-3$, &c., it is always known whether $x-p$ be odd or even. The number of terms may be less; for if Q_x be zero, the number of terms would be the next whole number above $\frac{1}{3}(x-p)$, &c.

That the equation

$$u_x=c(P_x...P_{p+1})N_{x,p}$$

is a complementary solution of the original equation, or in other words, a solution of the original equation wanting the term G_x, may be directly verified; for we have

$$u_x-P_xu_{x-1}=c(P_x..P_{p+1})(N_{x,p}-N_{x-1,p})$$
$$=c(P_x..P_{p+1})\Delta N_{x-1,p}.$$

Now $\Delta N'_{x-1,p}=0$,

$$\Delta N''_{x-1,p}=q_x+r_x+s_x+..+z_x,$$

$$\Delta N'''_{x-1,p}=q_xN''_{x-2,p}+r_xN''_{x-3,p}+s_xN''_{x-4,p}+...+w_xN''_{x-n+1,p}+z_xN''_{x-n,p},$$

and generally

$$\Delta N_{x-1,p}^{(a+1)}=q_xN_{x-2,p}^{(a)}+r_xN_{x-3,p}^{(a)}+s_xN_{x-4,p}^{(a)}+...+w_xN_{x-n+1,p}^{(a)}+z_xN_{x-n,p}^{(a)},$$

whence

$$\Delta N_{x-1,p}=q_xN_{x-2,p}+r_xN_{x-3,p}+s_xN_{x-4,p}+..+w_xN_{x-n+1,p}+z_xN_{x-n,p},$$

and

$$u_x-P_xu_{x-1}=Q_xu_{x-2}+R_xu_{x-3}+S_xu_{x-4}+..+W_xu_{x-n+1}+Z_xu_{x-n}.$$

In this part of the solution, I apprehend that it will not generally be necessary to have regard to the lower limits, since p may have any constant value, and that value may be taken which is most convenient in each case; and if we make $p=-\infty$, all the lower limits will have this value.

This part of the solution would then be

$$u_x=cP_x\ldots P_1\{1+A_x+B_x+C_x+..\},$$

where

$$A_x=\Sigma q_{x+1}+\Sigma r_{x+1}+\Sigma s_{x+1}+..+\Sigma w_{x+1}+\Sigma z_{x+1};$$

and generally each term of the part within the brackets is formed from the preceding term thus: first change x into $x-1$, multiply by q_{x+1}, and effect a summation; then change (in such preceding term) x into $x-2$, multiply by r_{x+1}, and effect a summation; and so on until lastly we change x into $x-n+1$, multiply by z_{x+1}, and effect a summation; and the sum of the parts thus obtained is the next term.

The verification of the particular solution is easily derived from the above; but it rests on the assumption that the algebraic value above given for $s^n(P_x..P_{p+1})$ is correct; to which therefore particular attention is directed.

The equation

$$u_x=cs^n(P_x..P_{p+1}),$$

considered as a solution of the original equation wanting the term G_x, implies that

$$s^n(P_x..P_{p+1})=P_xs^n(P_{x-1}..P_{p+1})+Q_xs^n(P_{x-2}..P_{p+1})+R_xs^n(P_{x-3}..P_{p+1})+..+Z_xs^n(P_{x-n}..P_{p+1}).$$

Now in order to verify the particular solution,

$$u_x=G_x+P_xG_{x-1}+s^n(P_xP_{x-1})G_{x-2}+s^n(P_xP_{x-1}P_{x-2})G_{x-3}+..+s^n(P_x..P_{x-p+1})G_{x-p}+\ldots,$$

it is only requisite that

$$s^n(P_x..P_{x-p+1})=P_xs^n(P_{x-1}..P_{x-p+1})+Q_xs^n(P_{x-2}..P_{x-p+1})+R_xs^n(P_{x-3}..P_{x-p+1})+..+Z_xs^n(P_{x-n}..P_{x-p+1});$$

and this is true, for it is identical in form with the equation last above given, notwithstanding the occurrence of x in the lowest value of P, for this lowest value remains the same throughout the expression.

7. If $P_x=0$, the expressions $s^n(P_x\ldots P_{x-m})$ reduce themselves to those terms which do not contain any value of P. It would not be difficult to determine generally what terms these are; but probably the most convenient general method of arriving at the solution in an algebraical form would be to make P_x equal to a constant b, and to make b equal to zero in the result finally obtained.

8. The above particular solution of the original equation is in such a form that the general term of the indefinite series representing the solution is given in explicit terms; but that general term may be represented in an implicit form, which perhaps is more convenient for practical use.

By attending to the formation of the successive expressions $s^n(P_x\ldots P_m)$, it will readily be seen that the series

$$M_0G_x+M_1G_{x-1}+M_2G_{x-2}+..+M_pG_{x-p}+..$$

is a solution of the original equation, if

$$M_0=1,$$
$$M_1=P_1M_0,$$
$$M_2=P_{2-1}M_1+Q_2M_0,$$
$$M_3=P_{3-2}M_2+Q_{3-1}M_1+R_3M_0,$$
$$\cdots\quad\cdots\quad\cdots\quad\cdots$$
$$\cdots\quad\cdots\quad\cdots\quad\cdots$$
$$\cdots\quad\cdots\quad\cdots\quad\cdots$$
$$M_p=P_{s-p+1}M_{p-1}+Q_{s-p+2}M_{p-2}+R_{s-p+3}M_{p-3}+\ldots+W_{s-p+n-1}M_{p-n+1}+Z_{s-p+n}M_{p-n};$$

which last is a general relation determining the coefficient of any term from the coefficients of the n preceding terms; or from the coefficients of all the preceding terms when the number of these preceding terms is less than n. This relation is the equation of formation, and may be regarded as universal, bearing in mind that when p is less than n some of the terms of this relation vanish.

The solution of the original equation is therefore reduced to that of a similar equation without second member: and, by what has preceded, this solution is

$$M_p=\varepsilon^v(P_{s-p+1},\ldots P_s),$$

it being understood that $M_0=1$; and this is the value of M_p before given.

But the value of M_p may be found otherwise, thus:

Make $$P_{s-p+1}=P'_p,\ Q_{s-p+2}=Q'_p,\ \&c.\ \&c.$$

Then the solution is evidently

$$M_p=\varepsilon^v(P'_p..P'_1),$$

where the operation v has the same meaning as before, except that it is applied to the accented letters.

Consequently

$$M_p=(P'_p..P'_1)\{1+A_p+B_p+C_p+..\},$$

where

$$A_p=\Sigma_1q'_{p+1}+\Sigma_2r'_{p+1}+..+\Sigma_{s-1}z'_{p+1},$$
$$B_p=\Sigma_3(q'_{p+1}A_{p-1})+\Sigma_4(r'_{p+1}A_{p-2})+\ldots+\Sigma_{2s-1}(z'_{p+1}A_{p-s+1}),$$

and generally the terms are formed as stated in section 5, using p for x.

9. I shall conclude this part of the subject with a few simple examples for the purpose of illustrating the processes here given.

Ex. 1. Let the equation be

$$u_x=au_{x-1}+b^3u_{x-3}+G_x.$$

That part of the solution which is independent of G_x, is

$$u_x=c\{a^x+(x-1)a^{x-3}b^3+\frac{1}{2}(x-2)(x-3)a^{x-4}b^4+\frac{1}{2.3}(x-3)(x-4)(x-5)a^{x-6}b^5+\ldots\};$$

and since in the present case P_x and Q_x are constants, we have

$$M_p=a^p+(p-1)a^{p-2}b^2+\frac{1}{2}(p-2)(p-3)a^{p-4}b^4+\frac{1}{2.3}(p-3)(p-4)(p-5)a^{p-6}b^6+\ldots$$

whence the particular value of u_x is a series of terms of the form

$$G_x+aG_{x-1}+(a^2+b^2)G_{x-2}+(a^3+2ab^2)G_{x-3}+(a^4+3a^2b^2+b^4)G_{x-4}+(a^5+4a^3b^2+3ab^4)G_{x-5}+\ldots$$

The difference in character between the solution proposed in this paper, and that which would result from a perfect analysis of the general equation, may be exemplified by the present instance.

The perfect solution of this equation is known to be

$$u_x=\frac{1}{\alpha-\beta}\left(\alpha^x\Sigma\frac{G_{x+2}}{\alpha^{x+1}}-\beta^x\Sigma\frac{G_{x+2}}{\beta^{x+1}}\right),$$

where α and β are the roots of $t^2-at-b^2=0$, and each Σ introduces a constant. Now if the constants be made equal, and the expression be written at length, we shall obtain the form derived above.

The expansion of the two terms within the parenthesis gives

$$G_{x+1}+\alpha G_x+\alpha^2G_{x-1}+\ldots+\alpha^{p+1}G_p+\ldots+c\alpha^x$$

and

$$G_{x+1}+\beta G_x+\beta^2G_{x-1}+\ldots+\beta^{p+1}G_p+\ldots+c\beta^x;$$

and if the difference of these be divided by $\alpha-\beta$, we get

$$G_x+\frac{\alpha^2-\beta^2}{\alpha-\beta}G_{x-1}+\ldots+\frac{\alpha^{p+1}-\beta^{p+1}}{\alpha-\beta}G_p+\ldots+c\frac{\alpha^x-\beta^x}{\alpha-\beta},$$

which is the same in effect as the result which we have obtained.

Ex. 2. Let the equation be

$$u_x=xu_{x-1}+au_{x-2}.$$

Then

$$u_x=c\Gamma(x+1)\left\{1+a\Sigma^x\frac{1}{x(x+1)}+a^2\Sigma^x\left(\frac{1}{x(x+1)}\Sigma^{x-1}\frac{1}{x(x+1)}\right)+\ldots\right\}$$

$$=c\Gamma(x+1)\left\{1-a\frac{1}{x}+a^2\frac{1}{(x-1)x}-\frac{a^3}{2.3}\frac{1}{(x-2)(x-1)x}+\ldots\right\}$$

$$=c\left\{\Gamma(x+1)-a\Gamma x+\frac{a^2}{2}\Gamma(x-1)-\frac{a^3}{2.3}\Gamma(x-2)+\ldots\right\};$$

which may be put under the form of the definite integral

$$u_x=c\int_0^\alpha e^{-v-\frac{a}{v}}v^x\,dv.$$

If we add a second member G_x, the equation for determining M_p is

$$M_p=(x-p+1)M_{p-1}+aM_{p-2};$$

whence

$$\mathrm{M}_p = x\ldots(x-p+1)\Big\{1+a\Sigma_1^p\frac{1}{(x-p+1)(x-p)}+a^2\Sigma_3^p\Big(\frac{1}{(x-p+1)(x-p)}\Sigma_1^{p-1}\frac{1}{(x-p+1)(x-p)}\Big)+\ldots\Big\}$$

$$= x\ldots(x-p+1)\Big\{1+a\Big(\frac{1}{x-p+1}-\frac{1}{x}\Big)$$

$$+a^2\Big(\frac{1}{2}\Big(\frac{1}{(x-p+2)(x-p+1)}-\frac{1}{(x-1)(x-2)}\Big)-\frac{1}{x}\Big(\frac{1}{x-p+1}-\frac{1}{x-2}\Big)\Big)+..\Big\}$$

from which the series for u_x can be expressed.

Ex. 3. Let the equation be

$$u_x = au_{x-1}+xu_{x-2}.$$

Then

$$u_x = c a^x\Big\{1+\frac{1}{a^2}\Sigma^x(x+1)+\frac{1}{a^4}\Sigma^x\big((x+1)\Sigma^{x-1}(x+1)\big)+\ldots\Big\}$$

$$= c\Big\{a^x+\frac{1}{2}x(x+1)a^{x-2}+\frac{1}{2.4}(x+1)x(x-1)(x-2)a^{x-4}+\frac{1}{2.4.6}(x+1)x\ldots(x-4)a^{x-6}+..\Big\}.$$

Ex. 4. Let the equation be

$$u_x = \frac{n}{x}u_{x-1}+c^2u_{x-2}.$$

Then

$$u_x = \frac{n^x}{\Gamma(x+1)}\Big\{1+\frac{c^2}{x^2}\Sigma^x x(x+1)+\frac{c^4}{x^4}\Sigma^x(x(x+1)\Sigma^{x-1}x(x+1))+..\Big\}$$

$$= \frac{n^x}{\Gamma(x+1)}\Big\{1+\frac{c^2}{x^2}\frac{1}{3}(x-1)x(x+1)$$

$$+\frac{c^4}{x^4}\Big(\frac{1}{6}(x+1)x(x-1)(x-2)(x-3)(x-4)+\frac{3}{5}(x+1)x(x-1)(x-2)(x-3)\Big)+..\Big\}.$$

Ex. 5. Let the equation be

$$u_x = \mathrm{P}_x u_{x-1}+x\mathrm{P}_x\mathrm{P}_{x-1}u_{x-2}+\mathrm{G}_x.$$

Here

$$q_x = x,\ \mathrm{N}'_{x,p}=1,\ \mathrm{N}''_{x,p}=\frac{x(x+1)}{2}-\frac{(p+1)(p+2)}{2},$$

$$\mathrm{N}'''_{x,p} = \frac{(x+1)x(x-1)(x-2)}{2.4}-\frac{(p+2)(p+1)}{2}.\frac{(x+1)x}{2}+\frac{(p+4)(p+3)(p+2)(p+1)}{2.4},$$

$$\mathrm{N}^{(iv)}_{x,p} = \frac{(x+1)x(x-1)(x-2)(x-3)(x-4)}{2.4.6}-\frac{(p+2)(p+1)}{2}.\frac{(x+1)x(x-1)(x-2)}{2.4}$$

$$+\frac{(p+4)(p+3)(p+2)(p+1)}{2.4}.\frac{(x+1)x}{2}-\frac{(p+6)(p+5)(p+4)(p+3)(p+2)(p+1)}{2.4.6},$$

$$\mathrm{N}^{(m+2)}_{x,p} = \frac{(x+1)..(x-2m)}{2.4..(2m+2)}-\frac{(p+2)(p+1)}{2}.\frac{(x+1)..(x-2m+2)}{2.4..2m}+\frac{(p+4)..(p+1)}{2.4}.\frac{(x+1)..(x-2m+4)}{2.4..(2m-2)}$$

$$+..\pm\frac{(p+2m)..(p+1)}{2.4..2m}.\frac{(x+1)x}{2}\mp\frac{(p+2m+2)..(p+1)}{2.4..(2m+2)}.$$

The particular solution, therefore, is

$$u_x = G_x + P_x G_{x-1} + (1+x) P_x P_{x-1} G_{x-2} + 2x P_x P_{x-1} P_{x-2} G_{x-3} + (x^3+x-2)(P_x..P_{x-3}) G_{x-4}$$
$$+ (3x^3-5x-2)(P_x..P_{x-4}) G_{x-5} + (x^3-11x+6)(P_x..P_{x-5}) G_{x-6} + \ldots;$$

and the part of the general solution found by this method is

$$u_x = c(P_x..P_0)\left(1 + \frac{(x+1)x}{2} + \frac{(x+1)...(x-2)}{2.4} + \frac{(x+1)...(x-4)}{2.4.6} + \ldots\right).$$

Ex. 6. Let the equation be

$$u_x + a_1 P_x u_{x-1} + a_2 P_x P_{x-1} u_{x-2} + .. + a_n (P_x..P_{x-n+1}) u_{x-n} = G_x;$$

then the equation for determining M_p is

$$M_p + a_1 P_{x-p+1} M_p + a_2 P_{x-p+1} P_{x-p+2} M_{p-2} + .. + a_n (P_{x-p+1}..P_{x-p+n}) M_{p-n} = 0;$$

or making

$$P_{x-p+1} = P'_p,$$

$$M_p + a_1 P'_p M_{p-1} + a_2 P'_p P'_{p-1} M_{p-2} + .. + a_n (P'_p..P'_{p-n+1}) M_{p-n} = 0;$$

the solution of which is evidently the solution of

$$M_p + a_1 M_{p-1} + a_2 M_{p-2} + .. + a_n M_{p-n} = 0,$$

multiplied by $(P'_p..P'_1)$.

Let $$(t^n + a_1 t^{n-1} + a_2 t^{n-2} + .. + a_n)^{-1} = \frac{A}{t-\alpha} + \frac{B}{t-\beta} + \ldots,$$

then $$M_p = (P'_p..P'_1)\{c_1 A \alpha^{p+n} + c_2 B \beta^{p+n} + ..\};$$

and taking the parts affected by each constant separately, it will be seen that the original equation reduces itself to a set of equations of the first order,

$$v_x - \alpha P_x v_{x-1} = \alpha^{n-1} A G_x,$$
$$v_x - \beta P_x v_{x-1} = \beta^{n-1} B G_x,$$
$$\ldots \quad \ldots \quad \ldots$$

so that its complete solution can be adequately represented.

Solution of Differential Equations in Series.

10. I now proceed to point out a method by which the processes above indicated may be made to give solutions of certain general forms of linear differential equations.

In a paper on Linear Differential Equations presented by me to the Royal Society, and which the Society has done me the honour to publish in the Philosophical Transactions (Part I. for 1848, p. 31), I have enunciated, and so far as is material to the present purpose, demonstrated the following theorem :—

That if, in a linear differential expression $\phi(x, D)u = X$ and its solution $u = \psi(x, D)X$, the letter x be changed into the operative symbol D and D into $-x$, we shall thus

obtain another linear differential expression $\varphi(D,-x)u=X$, the solution of which will be $u=\psi(D,-x)X$.

In the application of this theorem, care must be taken that the first-mentioned solution is so written that the operations included under the function ψ are not suppressed; and it must also be borne in mind that the expressions obtained by this interchange of symbols will not in all cases be obviously interpretable.

For applications of this singular analytical process I beg leave to refer to the memoir above cited, where it is employed for the solution, in finite terms, of extensive classes of linear differential equations, and equations in finite differences. So far as the process is legitimate, it is to be observed that it is founded on reasoning of a purely analytical character. It does not in any manner whatever flow from the calculus of operations, or depend for its validity upon the soundness of the logical basis on which this calculus rests.

Now it is a remarkable property of this mechanical interchange of symbols, that it instantaneously converts a linear equation in finite differences into a linear differential equation; so that wherever the former is soluble, the latter is soluble also, provided the result be intelligible, a condition always satisfied when the functions employed are rational algebraical functions.

As an instance worthy of notice, let us take the example last above given (*Ex.* 6.). Bearing in mind that $u_{x-n}=\epsilon^{-nD}u_x$, the proposed interchange gives the equation (writing φx for P_x),

$$u+a_1\varphi(D)(\epsilon^a u)+a_2\varphi(D)\varphi(D-1)(\epsilon^{2a}u)+..+a_n\varphi(D)..\varphi(D-n+1)(\epsilon^{na}u)=G;$$

whose solution, therefore, depends upon that of

$$v-\alpha\varphi(D)(\epsilon^a v)=\alpha^{n-1}AG,$$

a proposition established by Mr. Boole by the methods of the Calculus of Operations.

I propose, therefore, now to employ this theorem of the interchange of symbols for the purpose of converting the forms of solution, above given, of equations in finite differences into the particular solutions of some general forms of differential equations; viz. those equations whose factors do not contain any irrational or transcendental functions of x, or contain them only in the form of series of ascending powers of x.

11. Mr. Boole, in his General Method in Analysis, has shown that expressions of this character may be placed in the form

$$f_0(D)u+f_1(D)(\epsilon^\theta u)+f_2(D)(\epsilon^{2\theta}u)+..=U,$$

by changing the independent variable from x to its logarithm θ, and making use of the relation, $\left(D \text{ being } \frac{d}{d\theta}\right)$,

$$D(D-1)..(D-n+1)u=x^n\left(\frac{d}{dx}\right)^n u.$$

Making use of this relation, we immediately convert our equation, which we assume to be in the form

$$(a_n+b_nx+..+k_nx^{p-1}+l_nx^p+..)\frac{d^nu}{dx^n}+(a_{n-1}+b_{n-1}x+..+k_{n-1}x^{p-1}+l_{n-1}x^p+..)\frac{d^{n-1}u}{dx^{n-1}}$$
$$+....+(a_0+b_0x+..+k_0x^{p-1}+l_0x^p+..)u=G,$$

into

$$\left.\begin{aligned}a_n(D..(D-n+1))u+\quad b_n((D-1)...(D-n))(\epsilon^\theta u)+\quad c_n((D-2)...(D-n-1))(\epsilon^{2\theta}u)+...+\quad l_n((D-p)...(D-n-p+1))(\epsilon^{p\theta}u)+..\\ +a_{n-1}((D-1)..(D-n+1))(\epsilon^\theta u)+b_{n-1}((D-2)..(D-n\quad))(\epsilon^{2\theta}u)+....+k_{n-1}((D-p)..(D-n-p+2))(\epsilon^{p\theta}u)+..\\ +a_{n-2}((D-2)...(D-n+1))(\epsilon^{2\theta}u)+...+k_{n-2}((D-p)..(D-n-p+3))(\epsilon^{p\theta}u)+...\\ +\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad+..\end{aligned}\right\}=\epsilon^{n\theta}G.....(2.)$$

or

$$a_nu+\left(\frac{b_n(D-n)+a_{n-1}}{D}\right)(\epsilon^\theta u)+\left(\frac{c_n(D-n)(D-n-1)+b_{n-1}(D-n)+a_{n-2}}{D(D-1)}\right)(\epsilon^{2\theta}u)$$
$$+\left(\frac{d_n(D-n)(D-n-1)(D-n-2)+c_{n-1}(D-n)(D-n-1)+b_{n-2}(D-n)+a_{n-3}}{D(D-1)(D-2)}\right)(\epsilon^{3\theta}u)+...=(D..(D-n+1))^{-1}(\epsilon^{n\theta}G).$$

Now if in this equation we change D into θ and θ into $-D$, we obtain the equation in finite differences (which suppose to be of the nth order),

$$a_nu_\theta+\frac{b_n(\theta-n)+a_{n-1}}{\theta}u_{\theta-1}+\frac{c_n(\theta-n)(\theta-n-1)+b_{n-1}(\theta-n)+a_{n-2}}{\theta(\theta-1)}u_{\theta-2}+....=(\theta(\theta-1)..(\theta-n+1))^{-1}G_{\theta-n},$$

or

$$u_\theta+\frac{f_1\theta}{f_0\theta}u_{\theta-1}+\frac{f_2\theta}{f_0\theta}u_{\theta-2}+\frac{f_3\theta}{f_0\theta}u_{\theta-3}+....=(f_0\theta)^{-1}G_{\theta-n}=H_{\theta-n}\text{ (suppose)};$$

the solution of which, by section 8, is of the form

$$u_\theta=M_0H_{\theta-n}+M_1H_{\theta-n-1}+M_2H_{\theta-n-2}+..+M_mH_{\theta-n-m}+...,$$

where $M_0=1$,

$$M_1+\frac{f_1\theta}{f_0\theta}M_0=0,$$

$$M_2+\frac{f_1(\theta-1)}{f_0(\theta-1)}M_1+\frac{f_2\theta}{f_0\theta}M_0=0,$$

. . .

. . .

$$M_m+\frac{f_1(\theta-m+1)}{f_0(\theta-m+1)}M_{m-1}+\frac{f_2(\theta-m+2)}{f_0(\theta-m+2)}M_{m-2}+...+\frac{f_r(\theta-m+r)}{f_0(\theta-m+r)}M_{m-r}=0.$$

Restoring the symbols, and thereby converting $H_{\theta-n}$ into $\left(f_0(D)\right)^{-1}(\epsilon^{n\theta}G)$, which call H, we have

$$u=M_0H+M_1(\epsilon^\theta H)+M_2(\epsilon^{2\theta}H)+..+M_m(\epsilon^{m\theta}H)+...,$$

where M_0, M_1... denote a series of *operations* having the following significations and relations;—

$$M_0=1,$$

$$M_1+\frac{f_1(D)}{f_0(D)}M_0=0,$$

$$M_2+\frac{f_1(D-1)}{f_0(D-1)}M_1+\frac{f_2(D)}{f_0(D)}M_0=0,$$

. . . . . .

$$M_m+\frac{f_1(D-m+1)}{f_0(D-m+1)}M_{m-1}+\frac{f_2(D-m+2)}{f_0(D-m+2)}M_{m-2}+\ldots+\frac{f_r(D-m+r)}{f_0(D-m+r)}M_{m-r}=0;$$

or, by passing ε^θ, $\varepsilon^{2\theta}$, &c. outside the operations by the equation

$$\varphi(D)(\varepsilon^{m\theta}H)=\varepsilon^{m\theta}\varphi(D+m)H,$$

$$u=M_0H+\varepsilon^\theta M_1H+\varepsilon^{2\theta}M_2H+..+\varepsilon^{m\theta}M_mH+\ldots, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

where the general law of relation is

$$M_m+\frac{f_1(D+1)}{f_0(D+1)}M_{m-1}+\frac{f_2(D+2)}{f_0(D+2)}M_{m-2}+..+\frac{f_r(D+r)}{f_0(D+r)}M_{m-r}=0.$$

Now the expression H, which is the subject of all the operations, contains n arbitrary constants, since $f_0(D)$ is of the nth order; that is, provided a_n is not zero.

Let $\beta_1\ \beta_2\ldots\beta_n$ be the roots of $f_0t=0$; then the complete value of H is

$$(f_0(D))^{-1}(\varepsilon^{n\theta}G)+c_1\varepsilon^{\beta_1\theta}+c_2\varepsilon^{\beta_2\theta}+..+c_n\varepsilon^{\beta_n\theta};$$

of which the first term will give us the particular solution of the original equation, and each of the other terms a complementary solution. Bearing in mind the equation $\varphi(D)(\varepsilon^{p\theta})=\varphi p.\varepsilon^{p\theta}$, we see at once that the first complementary solution is

$$c_1\varepsilon^{\beta_1\theta}(A_0+A_1\varepsilon^\theta+A_2\varepsilon^{2\theta}+..+A_m\varepsilon^{m\theta}+..),$$

or

$$c_1x^{\beta_1}(A_0+A_1x+A_2x^2+..+A_mx^m+..),$$

where $A_0=1$, and the law of formation of the coefficients is

$$f_0(\beta_1+m)A_m+f_1(\beta_1+m)A_{m-1}+f_2(\beta_1+m)A_{m-2}+..+f_r(\beta_1+m)A_{m-r}=0;$$

and the remaining complementary solutions merely require the substitution of $\beta_2\ldots\beta_n$ successively for β_1, with new constants.

The reader will not fail to perceive the peculiarity of the series when a_n is unity, (which value it can always have when it is not zero); for in that case the roots of $f_0t=0$ are the natural numbers from 0 to $n-1$ inclusive, so that the series begin respectively with the terms 1, x, x^2, $\ldots x^{n-1}$.

If a_n be zero, that is, if the factor of the highest differential coefficient of u do not contain an absolute term, then in order that the transformed equation may take the form (2.), it will be necessary to pass ε^θ outside the operative functions in each term, and divide by ε^θ. The initial function f_0t will then be of the form

$$b_n(t\ldots(t-n+1))+a_{n-1}(t\ldots(t-n+2)),$$

and H will be

$$(f_0(D))^{-1}(\varepsilon^{(n-1)\theta}G).$$

Similarly, if in addition to a_n being zero, we have also b_n and a_{n-1} respectively equal to zero, it will be necessary to pass $\varepsilon^{2\theta}$ outside the operative functions, and divide by

$\epsilon^{\beta\theta}$; and so on if other terms of the factors are wanting. Thus we can in all cases obtain the transformed equation in the required shape; but in all the cases where coefficients thus vanish, there is the important qualification that $f_0 t$ is no longer necessarily of the nth order; so that H does not necessarily contain the proper number of arbitrary constants. The consequences of this consideration will be afterwards developed; in the meantime we proceed to consider what modifications the series undergo where $f_0 t$ has two or more equal roots.

12. If there should be two roots of $f_0 t = 0$ equal to β_1, one series will be deficient; and it will be supplied as follows. The expression H, or $(f_0(\mathrm{D}))^{-1}(\epsilon^{s\theta}\mathrm{G})$, contains in that case a term of the form $k_1 \theta \epsilon^{\beta_1 \theta}$; and it is easily seen that

$$\varphi(\mathrm{D})(\theta \epsilon^{\beta_1 \theta}) = \theta \varphi(\mathrm{D})(\epsilon^{\beta_1 \theta}) + \varphi'(\mathrm{D})(\epsilon^{\beta_1 \theta}).$$

The wanting series is, therefore,

$$k_1 x^{\beta_1}\{\log x(1 + \mathrm{A}_1 x + \mathrm{A}_2 x^2 + ..) + (\mathrm{A}'_1 x + \mathrm{A}'_2 x^2 + ..)\},$$

where

$$\mathrm{A}'_1 = \frac{d\mathrm{A}_1}{d\beta_1} \text{ \&c.}$$

If there should be three roots of $f_0 t = 0$ equal to β_1, two series will be deficient, one of which will be supplied as last mentioned; and the other by the introduction of the series

$$k_2 x^{\beta_1}\{(\log x)^2(1 + \mathrm{A}_1 x + \mathrm{A}_2 x^2 + ..) + 2 \log x(\mathrm{A}'_1 x + \mathrm{A}'_2 x^2 + ..) + (\mathrm{A}''_1 x + \mathrm{A}''_2 x^2 + ..)\},$$

where $\mathrm{A}''_1 = \frac{d^2\mathrm{A}_1}{d\beta_1^2}$ \&c.; for we have a term $k_2 \theta^2 \epsilon^{\beta_1 \theta}$; and it is easily seen that

$$\varphi(\mathrm{D})(\theta^2 \epsilon^{\beta_1 \theta}) = \theta^2 \varphi(\mathrm{D}) \epsilon^{\beta_1 \theta} + 2\theta \varphi'(\mathrm{D}) \epsilon^{\beta_1 \theta} + \varphi''(\mathrm{D}) \epsilon^{\beta_1 \theta}.$$

And generally since, where there are $p+1$ equal roots β_1, we have terms

$$c_1 \epsilon^{\beta_1 \theta} + k_1 \theta \epsilon^{\beta_1 \theta} + k_2 \theta^2 \epsilon^{\beta_1 \theta} + .. + k_p \theta^p \epsilon^{\beta_1 \theta};$$

and since

$$\varphi(\mathrm{D})(\theta^p \epsilon^{\beta_1 \theta}) = \theta^p \varphi(\mathrm{D}) \epsilon^{\beta_1 \theta} + p\theta^{p-1} \varphi'(\mathrm{D}) \epsilon^{\beta_1 \theta} + p \frac{p-1}{2} \theta^{p-2} \varphi''(\mathrm{D}) \epsilon^{\beta_1 \theta} + \ldots;$$

the deficient series will be supplied by the following, taken with a different constant for every value of p from unity upwards:

$$k_p x^{\beta_1}\Big\{(\log x)^p(1 + \mathrm{A}_1 x + \mathrm{A}_2 x^2 + ..) + p(\log x)^{p-1}(\mathrm{A}'_1 x + \mathrm{A}_2 x^2 + ..)$$

$$+ p\frac{p-1}{2}(\log x)^{p-2}(\mathrm{A}''_1 x + \mathrm{A}''_2 x^2 + ..) + .. + p \log x(\mathrm{A}_1^{(p-1)} x + \mathrm{A}_2^{(p-1)} x^2 + ..) + (\mathrm{A}_1^{(p)} x + \mathrm{A}_2^{(p)} x^2 + ..)\Big\}.$$

As a matter of convenience, when the equal roots are zero, a temporary nominal value should be given to them for the purpose of differentiating A_1, \&c.

13. Hitherto we have attended especially to the complementary solutions, or in other words, regarded G as zero. The operations, however, indicated in (3.) may be readily performed when G is a rational function of x; which we will suppose to be

cleared of fractions, and so cleared to consist of a set of terms $a_p x^p$. Then for this term $(f_0(D))^{-1}(\epsilon^{mp}G)=a_p(f_0(D))^{-1}\epsilon^{(n+p)p}=a_p(f_0(n+p))^{-1}\epsilon^{(n+p)p}$;
and we have, as before,

$$u=a_p x^{(n+p)}(B_0+B_1x+B_2x^2+..+B_mx^m+..),$$

where $B_0=1$, and the law of formation is

$$f_0(n+p+m)B_m+f_1(n+p+m)B_{m-1}+f_2(n+p+m)B_{m-2}+...=0;$$

and the whole solution is found by taking all the values of p. This will undergo a slight alteration, as the incipient term will be of the form $f_0(D)(\epsilon^{(n-r)p}G)$, where r factors of (2.) vanish by reason of some of the constant coefficients a_n, &c. being zero.

In like manner it would be easy to represent the series if G contained $\log x$ and its powers; but for most other forms it would be necessary to expand G in order to represent the series explicitly. The solution however is theoretically complete, since it consists solely in the performance of operations which are known explicit functions of D.

14. Before proceeding further with the main subject, I shall illustrate this process by a few examples.

Ex. 1. Let the equation be

$$(1+b_2x+c_2x^2)\frac{d^2u}{dx^2}+(a_1+b_1x)\frac{du}{dx}+a_0u=G.$$

Referring to (2.), we have

$$f_0D=D(D-1),\ f_1D=b_2(D-1)(D-2)+a_1(D-1),$$
$$f_2(D)=c_2(D-2)(D-3)+b_1(D-2)+a_0;$$

roots of $f_0t=0$ are 0 and 1.

First complementary series,

$$c_1(A_0+A_1x+A_2x^2+..+A_mx^m+..),$$

where

$A_0=1$, and $m(m-1)A_m+(b_2(m-1)(m-2)+a_1(m-1))A_{m-1}+(c_2(m-2)(m-3)+b_1(m-2)+a_0)A_{m-2}=0$
is the law of formation.

Second complementary series,

$$c_2x(A_0+A_1x+A_2x^2+..+A_mx^m+..),$$

where

$A_0=1$, and $(m+1)mA_m+(b_2(m)(m-1)+a_1m)A_{m-1}+(c_2(m-1)(m-2)+b_1(m-1)+a_0)A_{m-2}=0$
is the law of formation.

Particular solution,

$$u=\psi_0(D)H+\epsilon^p\psi_1(D)H+\epsilon^{2p}\psi_2(D)H+..+\epsilon^{mp}\psi_m(D)H+..,$$

where

$H=\left(\frac{d}{dx}\right)^{-2}G$, $\psi_0(D)=1$, and $f_0(D+m)\psi_m(D)+f_1(D+m)\psi_{(m-1)}(D)+f_2(D+m)\psi_{m-2}(D)=0$
is the law of the formation of the operative functions.

The three laws of formation, which are here written down at length, are in substance the same; for from the last the others are made by merely writing the roots successively in lieu of D in the factors.

Ex. 2. Let the equation be

$$(x^3+qx^4)\frac{d^2u}{dx^2}+(x+px^3+5qx^3)\frac{du}{dx}+(px-n^2+(4q+r)x^3)u=G.$$

Referring to (2.), we have in the first instance,

$$((D-2)^2-n^2)(\epsilon^{2x}u)+p(D-2)(\epsilon^{2x}u)+(q(D-4)D+4q+r)\epsilon^{4x}u=G,$$

whence

$$(D^2-n^2)u+pD(\epsilon^x u)+(qD^2+r)(\epsilon^{2x}u)=\epsilon^{-2x}G;$$

roots of $f_\epsilon t=0$ are n and $-n$.

First complementary series,

$$c_1x^n(A_0+A_1x+A_2x^2+..+A_mx^m+..),$$

where

$$A_0=1, \text{ and } ((n+m)^2-n^2)A_m+p(n+m)A_{m-1}+(q(n+m)^2+r)A_{m-2}=0$$

is the law of formation.

Second complementary series,

$$c_2x^{-n}(A_0+A_1x+A_2x^2+..+A_mx^m+..),$$

where the law is, as before, changing the sign of n.

Particular solution,

$$u=\psi_0(D)H+\epsilon^x\psi_1(D)H+..+\epsilon^{mx}\psi_m(D)H+..,$$

where

$$H=(D^2-n^2)^{-1}(\epsilon^{-2x}G),\ \psi_0(D)=1,$$

and

$$((D+m)^2-n^2)\psi_m(D)+p(D+m)\psi_{m-1}(D)+(q(D+m)^2+r)\psi_{m-2}(D)=0$$

is the law of the formation of the operative functions.

If $p=0$, $q=0$, and $r=1$, so that the equation becomes

$$x^2\frac{d^2u}{dx^2}+x\frac{du}{dx}+(x^2-n^2)u=0,$$

the law is

$$A_m=-\frac{A_{m-2}}{m(2n+m)},$$

whence

$$u=c_1x^n\left\{1-\frac{1}{4}(1+n)^{-1}x^2+\frac{1}{4.8}(1+n)^{-1}(2+n)^{-1}x^4-\frac{1}{4.8.12}(1+n)^{-1}(2+n)^{-1}(3+n)^{-1}x^6+\ldots\right\},$$

$$+c_2x^{-n}\left\{1-\frac{1}{4}(1-n)^{-1}x^2+\frac{1}{4.8}(1-n)^{-1}(2-n)^{-1}x^4-\frac{1}{4.8.12}(1-n)^{-1}(2-n)^{-1}(3-n)^{-1}x^6+\ldots\right\}.$$

Ex. 3. Let the equation be

$$x^3\frac{d^3u}{dx^3}+3x^2\frac{d^2u}{dx^2}+x\frac{du}{dx}+qx^2u=G.$$

Referring to (2.), we have

$$D^3u+qx^mu=G;$$

$f_0(D)=D^3$; three roots equal to zero;

$f_m(D)=q$;

$m^3A_m+qA_{m-m}=0$, law of formation.

Hence the complementary series are,

$$u=c_1\Big\{1-\frac{q}{n^3}x^m+\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}-\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+\ldots.\Big\}$$

$$+c_2\Big\{\log x\Big(1-\frac{q}{n^3}x^m+\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}-\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+\ldots\Big)$$

$$+3\Big(\frac{1}{n}\frac{q}{n^3}x^m-\Big(\frac{1}{n}+\frac{1}{2n}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}+\Big(\frac{1}{n}+\frac{1}{2n}+\frac{1}{3n}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+..\Big)\Big\}$$

$$+c_3\Big\{(\log x)^2\Big(1-\frac{q}{n^3}x^m+\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}-\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+..\Big)$$

$$+6\log x\Big(\frac{1}{n}\frac{q}{n^3}x^m-\Big(\frac{1}{n}+\frac{1}{2n}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}+\Big(\frac{1}{n}+\frac{1}{2n}+\frac{1}{3n}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+..\Big)$$

$$+6\Big(-\frac{2}{n^3}\frac{q}{n^3}x^m+\Big(\frac{2}{n^3}+\frac{2}{(2n)^3}+\frac{3}{n(2n)}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}x^{2m}$$

$$-\Big(\frac{2}{n^3}+\frac{2}{(2n)^3}+\frac{2}{(3n)^3}+\frac{3}{n(2n)}+\frac{3}{n(3n)}+\frac{3}{(2n)(3n)}\Big)\frac{q}{n^3}\frac{q}{(2n)^3}\frac{q}{(3n)^3}x^{3m}+..\Big)\Big\};$$

and the particular solution is

$$u=H-qx^m(D+n)^{-3}H+q^2x^{2m}(D+n)^{-3}(D+2n)^{-3}H-\ldots,$$

H being $D^{-3}(s^{3m}G)$.

15. The completeness of the preceding forms of solution depends, as above intimated, upon the circumstance that the function $f_0(D)$ is of an order not lower than the order of the original equation. It may however be of a lower order, as would take place in the first of the examples above given, if a_2 instead of being 1 were zero and b_2 were also zero.

Let the equation then be (*Ex.* 4.),

$$c_2x^2\frac{d^2u}{dx^2}+(1+b_1x)\frac{du}{dx}+a_0u=G.$$

Referring to (2.), we have, in the first instance,

$$(D-1)(s^0u)+\big(c_2(D-2)(D-3)+b_1(D-2)+a_0\big)\big(s^{2m}u\big)=G,$$

or

$$Du+\big(c_2(D-1)(D-2)+b_1(D-1)+a_0\big)\big(s^0u\big)=s^{-2}G;$$

so that $f_0(D)$ is of the first order, and the root is zero.

The only complementary function to be obtained is therefore

$$u=c_1\Big\{1-a_0x+\frac{1}{2}a_0(b_1+a_0)x^2-\frac{1}{2.3}a_0(b_1+a_0)(1.2c_2+2b_1+a_0)x^3$$

$$+\frac{1}{2.3.4}a_0(b_1+a_0)(1.2c_2+2b_1+a_0)(2.3c_2+3b_1+a_0)x^4-\ldots\Big\},$$

a series which is divergent, but which, as will also be seen afterwards, is finite when the constant coefficients are connected by the formula $(p-1)pc_2+pb_1+a_0=0$, p being any positive integer.

Further, it may happen that the series obtained by the process, even when they afford a complete solution in respect of the number of constants, are divergent for all or for some values of x. This may evidently be the case in the solution of the second of the examples above given; for the law of the coefficients, as we advance in the series, approximates to $A_m=-qA_{m-2}$.

In these cases, other solutions in series may be obtained by resolving the equation in finite differences in a series of terms of the form $H_{\theta+p}$ instead of $H_{\theta-p}$. In order to effect this, all that is necessary is to write $\theta+r$ for θ, (r being the order of the equation in finite differences), and to divide by the factor of the last term instead of the factor of the first term; or in other words, we must pass $\varepsilon^{r\theta}$ outside the functions in (2.), and multiply by $\varepsilon^{-r\theta}$; so that this equation now assumes the form

$$f_r(D)u+f_{r-1}(D)(\varepsilon^{-\theta}u)+f_{r-2}(D)(\varepsilon^{-2\theta}u)+\ldots=\varepsilon^{(n-r)\theta}G;$$

and the equation in finite differences is

$$f_r(\theta)u_\theta+f_{r-1}(\theta)u_{\theta+1}+f_{r-2}(\theta)u_{\theta+2}+\ldots=G_{\theta+r-n}.$$

We have now to inquire for the roots of $f_r t=0$; the incipient term is $(f_r(D))^{-1}(\varepsilon^{(n-r)\theta}G)$, which call H_1; and the particular solution will be found to be

$$u=\psi_0(D)H_1+\varepsilon^{-\theta}\psi_1(D)H_1+\varepsilon^{-2\theta}\psi_2(D)H_1+\ldots+\varepsilon^{-m\theta}\psi_m(D)H_1+\ldots,$$

where

$$\psi_0(D)=1, \text{ and } f_r(D-m)\psi_m(D)+f_{r-1}(D-m)\psi_{m-1}(D)+\ldots=0$$

is the law of the formation of the operative functions.

The substitution of the roots of $f_r t$ successively for D gives the law of formation of the complementary series.

Taking the last example, the transformed equation now becomes

$$(c_2D(D-1)+b_1D+a_0)u+(D+1)(\varepsilon^{-\theta}u)=\varepsilon^{-2\theta}G.$$

Let the roots of $f_r t$ or $c_2t(t-1)+b_1t+a_0=0$, be β_1 and β_2.

The first complementary series is

$$c_1x^{\beta_1}(A_0+A_1x^{-1}+\ldots+A_mx^{-m}+\ldots),$$

where $A_0=1$, and $f_r(\beta_1-m)A_m+(\beta_1-m+1)A_{m-1}=0$ is the law of formation; the series then are

$$c_1\left\{x^{\beta_1}-\frac{\beta_1}{f_r(\beta_1-1)}x^{\beta_1-1}+\frac{\beta_1}{f_r(\beta_1-1)}\frac{\beta_1-1}{f_r(\beta_1-2)}x^{\beta_1-2}-\frac{\beta_1}{f_r(\beta_1-1)}\frac{\beta_1-1}{f_r(\beta_1-2)}\frac{\beta_1-2}{f_r(\beta_1-3)}x^{\beta_1-3}+..\right\}$$

$$+c_2\{\text{ similar function of }\beta_2\quad\ldots\ldots\ldots\ldots\ldots\ldots\},$$

which is, (since $f_r(\beta_1-n)=n(n+1)c_2-2n\beta_1-nb_1$),

$$c_1\left\{x^{\beta_1}-\frac{\beta_1}{2c_2-2\beta_1-b_1}x^{\beta_1-1}+\frac{\beta_1}{2c_2-2\beta_1-b_1}\frac{\beta_1-1}{2.3c_2-4\beta_1-2b_1}x^{\beta_1-2}\right.$$

$$\left.-\frac{\beta_1}{2c_2-2\beta_1-b_1}\frac{\beta_1-1}{2.3c_2-4\beta_1-2b_1}\frac{\beta_1-2}{3.4c_2-6\beta_1-3b_1}x^{\beta_1-3}+..\right\}$$

$$+c_2\{\text{ similar function of }\beta_2\quad\ldots\ldots\ldots\ldots\}.$$

When β_1 or β_2 is a positive integer, one of these series is terminable; and if both are positive integers, the series derived from the smaller root is terminable, and the other gives no result, the coefficients becoming infinite. The first of the series will then be found to give the same result as that produced from the divergent series (which is evidently terminable in form in the case indicated), except that it begins at the other end. In this case the other complementary solution can be found in finite terms by reducing the order of the equation.

The particular solution is

$$u=H_1-x^{-1}\frac{D}{f_r(D-1)}H_1+x^{-2}\frac{D}{f_r(D-1)}\frac{D-1}{f_r(D-2)}H_1-\ldots,$$

H_1 being $(f_r(D))^{-1}(\epsilon^{-ax}G)$.

Let us now return to example 2, the solution of which, as above found, is in some cases divergent.

The transformed equation now becomes

$$(q(D+2)^2+r)u+p(D+2)(\epsilon^{-a}u)+((D+2)^2-r^2)(\epsilon^{-2a}u)=\epsilon^{-ax}G.$$

Roots of $f,t=0$ are $-2\pm\sqrt{\left(\frac{r}{q}\right)}$, which call β_1 and β_2.

First complementary series,

$$c_1x^{\beta_1}\left(A_0+\frac{A_1}{x}+\frac{A_2}{x^2}+..+\frac{A_m}{x^m}+..\right),$$

where

$A_0=1$, and $(q(\beta_1-m+2)^2+r)A_m+p(\beta_1-m+2)A_{m-1}+((\beta_1-m+2)^2-r^2)A_{m-2}=0$, is the law of formation; and the second complementary series is the same, using the other root with a different constant.

In like manner the particular solution is easily represented.

16. We are now in a position to discuss the character of the various series obtained by this process with reference to their convergency or divergency, a subject of the highest importance to the value of the process. The investigations which follow, will, it is apprehended, be found to afford a complete test of the nature of the series.

In general, it will of course be understood that these researches, as to convergency and divergency, relate only to the complementary series, or in other words, to equations deprived of their second member; nevertheless they will to a great extent, if not throughout, apply to cases in which the second member is in the form of integer powers of x or of $\log x$.

1st. When in the set of functions

$$f_0(D),\ f_1(D),\ f_2(D),\ldots f_{r-1}(D),\ f_r(D),$$

the function $f_0(D)$ is of a higher dimension with regard to D than any other of the set, or is what we shall here call the dominant function, the solution of the equation can always be found in a *convergent* series of ascending powers of x; and if in such a case we solve the equation in a series of descending powers of x, which we can do if we please, that series is certainly divergent.

This is immediately apparent from the consideration of the law of the coefficients

$$f_0(\beta_1+m)A_m+f_1(\beta_1+m)A_{m-1}+\ldots+f_r(\beta_1+m)A_{m-r}=0;$$

which, as m increases without limit, approaches to the form

$$A_m=-\frac{f_1m}{f_0m}A_{m-1}-\frac{f_2m}{f_0m}A_{m-2}-\ldots-\frac{f_rm}{f_0m}A_{m-r},\text{ or } mA_m=-a_{m-1}A_{m-1}-b_{m-1}A_{m-2}-\ldots,$$

assuming that all the functions are only one degree lower than A_m, which is the least favourable case for convergency. Therefore, if the largest of the terms of the right-hand side of this equation be $l_{m-1}A_{m-p}$, we have

$$A_m<\frac{rl_{m-1}}{m}A_{m-p};$$

and we can therefore arrive at a point in the series at which the ratio of the coefficient of x^m to that of x^{m-p} diminishes without limit.

It will also be observed that the series introduced by two or more equal roots are of the same character as the original series from which they are derived; for, A_m being of the form $\varphi(\beta_1+m)$, we have $\frac{dA_m}{d\beta_1}=\frac{dA_m}{dm}$; and when A_{m-p} is of a higher order with reference to m than A_m, $\frac{dA_{m-p}}{dm}$ is also of a higher order than $\frac{dA_m}{dm}$, and so for the other differential coefficients.

We have now merely to inquire what must be the form of the original equation that $f_0(D)$ may be the dominant function. Referring to (2.), we see that it is necessary that the factor of the highest differential coefficient of u should contain one term only. If this factor be 1 or x, no restriction need be imposed on the succeeding factors. If it be x^2, the factor of the next lower differential coefficient must not contain an absolute term; and generally, if x^p be the factor of $\frac{d^nu}{dx^n}$, the factor of $\frac{d^{n-1}u}{dx^{n-1}}$ must begin with a term not lower than x^{p-1}, that of $\frac{d^{n-2}u}{dx^{n-2}}$ with a term not lower than x^{p-2}, and so on.

In short, all equations where x does not enter into the factor of $\frac{d^n u}{dx^n}$, and all equations of the form

$$x^p \frac{d^n u}{dx^n} + (k_n x^{p-1} + l_n x^p + ..) \frac{d^{n-1} u}{dx^{n-1}} + (h_n x^{p-2} + ...) \frac{d^{n-2} u}{dx^{n-2}} + ... = 0,$$

where p is a positive integer, are soluble in *convergent* series of *ascending* powers of x. The third example above given is an instance of this form.

2ndly. When in the set of functions

$$f_r(\mathrm{D}),\ f_{r-1}(\mathrm{D}),\ \ldots f_1(\mathrm{D}),\ f_0(\mathrm{D}),$$

the function $f_r(\mathrm{D})$ is the dominant function, the solution of the equation can always be found in a *convergent* series of descending powers of x; and if in such a case we solve the equation in a series of ascending powers of x, that series is certainly divergent.

This is apparent, as before, from the consideration of the law of the coefficients,

$$f_r(\beta_1 - m)\mathrm{A}_m + f_{r-1}(\beta_1 - m)\mathrm{A}_{m-1} + \ldots + f_0(\beta_1 - m)\mathrm{A}_{m-r} = 0,$$

which, as m increases without limit, approaches to

$$m\mathrm{A}_m = h_{n-1}\mathrm{A}_{m-1} - k_{n-1}\mathrm{A}_{m-2} + \ldots$$

in the least favourable case for convergency.

On proceeding to inquire what must be the form of the original equation, we see again that it is necessary that the factor of the highest differential coefficient of u should contain one term only. If this be x^p, then the other restrictions are, that the factor of the next differential coefficient must stop at x^{p-1}, that of the next at x^{p-2}, and so on.

In short, for all integer values of p the equation

$$x^p \frac{d^n u}{dx^n} + (a_{n-1} + b_{n-1}x + .. + k_n x^{p-1}) \frac{d^{n-1} u}{dx^{n-1}} + (a_{n-2} + b_{n-2}x + .. + h_{n-2}x^{p-2}) \frac{d^{n-2} u}{dx^{n-2}} + \ldots = 0$$

is soluble in a *convergent* series of *descending* powers of x. The 4th example above given is an instance of this form.

3rdly. When in the set of functions

$$f_0(\mathrm{D}),\ f_1(\mathrm{D}),\ \ldots f_{r-1}(\mathrm{D}),\ f_r(\mathrm{D}),$$

the functions $f_0(\mathrm{D})$ and $f_r(\mathrm{D})$ are of the same dimensions, and are both dominant over all the other functions, the solution of the equation can be found in a series of ascending powers of x, which for some values of x is convergent, and for other values of x is divergent; and the solution can also be found in a series of descending powers of x which is divergent for all values of x for which the other series is convergent, and convergent for all values of x for which the other series is divergent.

For in the ascending series the law of the coefficients approaches the form, (the

coefficient of the highest power of m in $f_0 m$ being 1, and that in $f_r m$ being l_n,)

$$A_m = -l_n A_{m-r},$$

and in the descending series the law approaches to

$$l_n A_m = \pm A_{m-r}.$$

The former series is therefore convergent for all values of x numerically less than $(l_n)^{-\frac{1}{r}}$, and divergent for all values of x numerically greater than this limit; and the latter series is divergent for all values of x numerically greater than this quantity, and divergent for all values of x numerically less.

The equations to which this rule is applicable are of the forms, (p' being less than p,)

$$(x^{p'}+l_n x^p)\frac{d^n u}{dx^n}+(h'_{n-1}x^{p'-1}+..+k_{n-1}x^{p-1})\frac{d^{n-1}u}{dx^{n-1}}+(g_{n-2}x^{p'-2}+..+h_{n-2}x^{p-2})\frac{d^{n-2}u}{dx^{n-2}}+\ldots=0,$$

and

$$(a_n+l_n x^p)\frac{d^n u}{dx^n}+(a_{n-1}+b_{n-1}x+..+k_{n-1}x^{p-1})\frac{d^{n-1}u}{dx^{n-1}}+(a_{n-2}+..+h_{n-2}x^{p-2})\frac{d^{n-2}u}{dx^{n-2}}+\ldots=0.$$

The second example above given is an instance of the first of these forms.

4thly. When in the set of functions

$$f_0(\mathrm{D}),\ f_1(\mathrm{D}),\ldots f_{r-1}(\mathrm{D}),\ f_r(\mathrm{D}),$$

one or more of the intermediate functions is or are of the same order as the extreme functions $f_0(\mathrm{D})$ and $f_r(\mathrm{D})$, or as the highest of these two when they differ in dimensions, the series obtained by the above processes will be divergent for some values of x, and we have not as yet any method of deriving a convergent series corresponding to these values; and if one or more of the intermediate functions be of a higher dimension than the extreme functions, the series obtained by the above processes will certainly be divergent.

These remaining cases therefore sever into two species; first, where some of the intermediate functions are of the same order as the highest of the extreme functions; secondly, where one or more of the intermediate functions are dominant.

The first of these species includes equations of the two following forms:—

$$(a_n x^{p'}+b_n x^{p'+1}+..+l_n x^p)\frac{d^n u}{dx^{n-1}}+(a_{n-1}x^{p'-1}+b_{n-1}x^{p'}+..)\frac{d^{n-1}u}{dx^{n-1}}+..+(a_r x^{p'-n}+\ldots)u=0,$$

in which there can be no function higher than $f_0(\mathrm{D})$; and

$$(a_n+b_n x+..+l_n x^p)\frac{d^n u}{dx^n}+(a_{n-1}+b_{n-1}x+..+k_{n-1}x^{p-1})\frac{d^{n-1}u}{dx^{n-1}}+\ldots=0,$$

in which there can be no function higher than $f_r(\mathrm{D})$.

In these cases it will easily be seen that the law of the coefficients of the ascending series, as m increases without limit, approximates to

$$a_n A_m+b_n A_{m-1}+\ldots+l_n A_{m-p}=0,$$

and the series therefore approaches without limit to a recurring series, in which the constants of relation are

$$-\frac{b_n}{a_n}x,\ -\frac{c_n}{a_n}x^2,\ \ldots\ -\frac{l_n}{a_n}x^p;$$

and the denominator of the rational fraction, to which the residue of the series approaches, is

$$\frac{1}{a_n}(a_n+b_nx+..+l_nx^p).$$

In the descending series, the law of the coefficients approximates to

$$l_nA_m+k_nA_{m-1}+..+a_nA_{m-p}=0,$$

and the series approaches without limit to a recurring series, in which the constants of relation are

$$-\frac{k_n}{l_n}\frac{1}{x},\ ..\ -\frac{b_n}{l_n}\frac{1}{x^{p-1}},\ -\frac{a_n}{l_n}\frac{1}{x^p};$$

and the denominator of the rational fraction, to which the residue of the series approaches, is

$$\frac{1}{l_nx^p}(a_n+b_nx+..+l_nx^p).$$

When $f_0(D)$ is higher than $f_r(D)$, the ascending series alone can be used; when $f_r(D)$ is higher than $f_0(D)$, the descending series alone can be used; and when $f_0(D)$ and $f_r(D)$ are of the same dimension, either may be used; and the approximations above referred to render it probable that these series, notwithstanding that they may be divergent, are the developments of continuous algebraical expressions.

The second of the species above referred to includes all equations which are excluded from the preceding forms; that is, all forms which transgress *both* the restrictions to which the equation in the third case is subjected.

Of these forms, the solutions, whether obtained in ascending or in descending series, are always divergent; and the divergency appears to be of an extreme and unmanageable character. In this case we have an intermediate dominant function; and the convergent solutions might, from considerations of analogy, be presumed to be series infinite in both directions, the roots of the dominant function determining the incipient terms.

The treatment of these forms requires the solution of the equation in finite differences

$$..+R_xu_{x+3}+Q_xu_{x+2}+P_xu_{x+1}+u_x+P_xu_{x-1}+Q_xu_{x-2}+R_xu_{x-3}+..=G_x,$$

not starting from either of the two extreme terms, as is done above, but from the term u_x, so as to get a result in the form

$$u_x=..+M_{-2}G_{x+2}+M_{-1}G_{x+1}+M_0G_x+M_1G_{x-1}+M_2G_{x-2}+..$$

It would probably not be difficult to show that such a solution exists; but I have not found one in a form available for the purpose to which it is desired to be applied.

17. Throughout the preceding investigations, the series obtained by the processes here displayed undergo a modification of form in the event of the expression $f_0 t$ or $f_1 t$, as the case may be, having one or more sets of imaginary roots.

Let there be a couple of such roots of the form $\alpha \pm \beta\sqrt{-1}$. In the ascending series these roots give

$$c_1 x^{\alpha+\beta\sqrt{-1}}(A_0+A_1x+A_2x^2+..+A_mx^m+..)$$
$$c_2 x^{\alpha-\beta\sqrt{-1}}(B_0+B_1x+B_2x^2+..+B_mx^m+..),$$

where

$$f_0(\alpha+m+\beta\sqrt{-1})A_m+f_1(\alpha+m+\beta\sqrt{-1})A_{m-1}+\ldots=0$$

and

$$f_0(\alpha+m-\beta\sqrt{-1})B_m+f_1(\alpha+m-\beta\sqrt{-1})B_{m-1}+\ldots=0$$

are the respective laws of formation.

It is apparent, therefore, that if A_m be of the form $\phi(\alpha+\beta\sqrt{-1})$, B_m is of the form $\phi(\alpha-\beta\sqrt{-1})$.

Making $c_2=c_1$, and remembering that

$$x^{\beta\sqrt{-1}}+x^{-\beta\sqrt{-1}}=2\cos(\beta\log x)$$
$$x^{\beta\sqrt{-1}}-x^{-\beta\sqrt{-1}}=2\sqrt{-1}\sin(\beta\log x),$$

the sum of the two series gives the double series,

$$2c_1x^\alpha\Big(\cos(\beta\log x)\{A_0+B_0+(A_1+B_1)x+..+(A_m+B_m)x^m+..\}$$
$$+\sqrt{-1}\sin(\beta\log x)\{A_0-B_0+(A_1-B_1)x+..+(A_m-B_m)x^m+..\}\Big);$$

which is necessarily real, since A_m+B_m is purely real, and A_m-B_m is purely imaginary.

Making now $c_1=-c_2$, the sum of the two series gives another double series, (making $c_2=-k\sqrt{-1}$,)

$$2kx^\alpha\Big(\sqrt{-1}\cos(\beta\log x)\{A_0-B_0+(A_1-B_1)x+..+(A_m-B_m)x^m+..\}$$
$$+\sin(\beta\log x)\{A_0+B_0+(A_1+B_1)x+..+(A_m+B_m)x^m+..\}\Big),$$

which is likewise real.

The descending series may be treated in a similar manner.

18. Most of the examples to which the preceding processes are applied have been taken from the paper in the Philosophical Transactions for 1844, in which Mr. Boole developed his new General Method in Analysis, with which the subject matter of the present paper is closely connected, though the methods exhibited are distinct; unless indeed it should prove, that the interchange of the symbol of operation and the independent variable, and the general relation exhibited by Mr. Boole's fundamental theorem of development connecting any system of linear differential equations with a corresponding system of equations in finite differences, are merely different representations of a part of some more general method or process.

The principal difference in results, so far as concerns the solution in series of linear differential equations, appears to be, that in this paper the law of relation of the

coefficients of each series is distinct, and substantially the same in form for all; and that it is not necessary to have recourse to the method of parameters in the cases of equal roots, or in the case of there being a term G on the right-hand side of the equation. In the case of imaginary roots, the laws of the series are in the first instance distinct from each other, and afterwards combined in couples.

19. The investigations contained in the latter part of this paper reduce the problem of the integration in finite terms of the general linear differential equation with rational coefficients, to the finding of an algebraical expression representing the development

$$A_0+A_1x+A_2x^2+\ldots.+A_mx^m+\ldots,$$

where $A_0=1$, and the law of relation is

$$f_0mA_m+f_1mA_{m-1}+f_2mA_{m-2}+\ldots+f_rmA_{m-r}=0;$$

the functions $f_0f_1f_2\ldots f_r$ being known specific functions. The series to be summed closely resembles a recurring series; it differs from it in this particular, that the law of relation, instead of being constant, has a uniform and simple variation as it progresses along the series. If the rational coefficients should be themselves infinite series, the process still applies, the only difference being that each term would be formed from all the preceding terms, instead of being formed from the r immediately preceding terms, or from all the preceding terms when the number of them is less than r.

In those cases in which the equation is soluble in finite terms by known methods, we are enabled to assign the algebraical expression for the series; a result which may be used for the discovery of generating functions.

Thus, taking the general equation of the first order,

$$(a_1+b_1x+c_1x^2+\ldots+l_1x^n)\frac{du}{dx}+(a_0+b_0x+c_0x^2+\ldots+k_0x^{n-1})u=0,$$

we see that

$$\varepsilon^{-\int_0^x\frac{a_0+b_0x+\ldots+k_0x^{n-1}}{a_1+b_1x+\ldots+l_1x^n}dx}=A_0+A_1x+A_2x^2+\ldots+A_mx^m+\ldots,$$

where $A_0=1$, and the general law of the series is

$$a_1mA_m+(b_1(m-1)+a_0)A_{m-1}+(c_1(m-2)+b_0)A_{m-2}+\ldots(l_1(m-n)+k_0)A_{m-n}=0.$$

If we take the general equation of the second order,

$$(a_2+b_2x+\ldots+l_2x^n)\frac{d^2u}{dx^2}+(a_1+b_1x+\ldots+k_1x^{n-1})\frac{du}{dx}+(a_0+b_0x+\ldots+h_0x^{n-2})u=0,$$

the law of the series will be

$$a_2m(m-1)A_m+(b_2(m-1)(m-2)+a_1(m-1))A_{m-1}+(c_2(m-2)(m-3)+b_1(m-2)+a_0)A_{m-2}+\ldots$$
$$+(l_2(m-n)(m-n-1)+k_1(m-n)+h_0)A_{m-n}=0;$$

and generally, in equations of the nth order, the law of relation involves the nth power of m, the number of the term sought for. Thus the determination of soluble

cases of linear equations resolves itself into the inquiry, in what cases can a series whose scale is of the nth order be resolved into a number of series whose scale is of the first order.

20. I have not thought it necessary here to extend these solutions in series to linear partial differential equations. The process by which the extension can be made is well known, and has no peculiar relation to the methods here developed.

XIV. *Electro-Physiological Researches.—Eighth Series.* *By Signor* CARLO MATTEUCCI. *Communicated by* W. R. GROVE, *Esq., F.R.S.*

Received September 10, 1849,—Read January 10, 1850.

I PROPOSED to myself in my former memoirs* to embrace under some general views the phenomena of muscular contraction, of the production of electricity in fishes, and of the relation between the electric current and nervous force. I shall now endeavour to redeem my pledge, thankful to Providence in being permitted to resume my studies, and to seek in them some alleviation of the profound grief occasioned by the recent disasters of my country.

Previously to giving an account of my recent researches, it will be advisable to recall, in a few words, the leading results which may be said to form the summary of my former studies on electro-physiology, and which have been the starting-point of my later investigations.

1. A constant development of electricity takes place in all animal tissues, and principally in the muscles. All the laws of the muscular current, which have been established by a great number of experiments, lead to the conclusion that this development of electricity is owing to the chemical actions of nutrition, and particularly to that of muscular fibre on arterial blood. This electro-physiological phenomenon is therefore simply dependent on a general physical law: we may compare a muscle in which arterial blood circulates, conveying thither the elements of nutrition, to a collection of particles of zinc surrounded by acidulated water. The two electricities separate, and are reunited instantaneously between the molecules of metal and of liquid. If we establish a circuit between muscular tissues and the parts which communicate with them, which do not suffer the same chemical action on the part of the blood, we obtain signs of an electric current the direction of which is already determined by the physical conditions of this source of electricity.

2. In each prism of the electrical organ of fishes, the two electricities are separated under the influence of nervous action propagated from the brain towards the extremities of the nerves: a relation exists between the direction and the intensity of the nervous current, and also between the position and the quantity of the two electricities developed in the prism: according to this relation, verified by experiment, if we represent (as AMPÈRE did for electro-magnetic action) the nervous current by the figure of a man extended on the nerve and looking towards the tail of the torpedo, or the dorsal surface of the gymnotus, the positive electricity of the prism

* Phil. Trans. 1847.

is found invariably to the left of the man. We may account for the position of the poles at the extremities of each prism, and the intensity of the discharge being proportionate with the length of the prisms, by the fact that each prism of the organ is a temporary electrical apparatus, as has been proved by numerous experiments.

3. It is proved by experiments that the strictest analogy exists between the discharge of electrical fishes and muscular contraction; there is not a circumstance which modifies one of these phenomena without acting equally on the other.

4. The contraction of a muscle developes in the nerve with which it is in contact, the cause by means of which the nerve excites contractions in the muscle through which it is ramified. Although it has not been possible as yet to decide by experiment whether this phenomenon ought to be considered as a case of nervous induction, or as the proof of an electric discharge produced by muscular contraction, we are compelled by analogy to adopt the latter hypothesis.

5. The electric current modifies the excitability of the nerve which it traverses, in a manner which differs greatly according to its direction: the electric current which is propagated in the same direction as the ramification of the nerve, destroys its excitability: the current which is propagated in a direction contrary to that of the ramification of the nerve, increases its sensibility: the phenomena excited by the cessation of the electric current which traverses the nerves of the animal, are produced by the modification which the excitability of the nerve has undergone by the passage of the current according to its direction: the voltaic alternatives are explained by the same cause, which is as follows:—the muscular contractions are excited by a current which is made to pass in a contrary direction to that in which its action is nullified.

After having thus briefly recapitulated the fundamental conclusions which I have scrupulously drawn from my lengthened researches in electro-physiology, I shall begin the exposition of my recent studies on this subject by describing some experiments the application of which I shall give in the sequel. I wished to satisfy myself whether the nervous filaments which conduct an electric current into a liquid, are capable, like metallic wires, of acting as electrodes and giving rise to the production of electro-chemical decomposition. In order to ascertain this point, I plunged in a solution of iodide of potassium two large nervous filaments taken from living animals, each of which was separately attached to the metallic extremities of a pile of fifteen couples. I did not obtain the slightest trace of electro-chemical decomposition. I concluded from this experiment that terminals formed of nervous filaments cannot serve to obtain electro-chemical decomposition, which appears to me to demonstrate that the conductibility of nervous matter is due to the liquid part of the matter itself.

I studied again the relative conductibility of the muscles to that of the nerves: I had already discovered that one might estimate the conductibility of the muscle as four times greater than that of the nervous substance. I had also found that a

hempen thread soaked in water, and a very fresh nervous filament, both being as nearly as possible of equal dimensions, presented resistances to the electric current in the proportion of 12 to 15. But the main object which I had in view in studying the relative conducting power of muscles and nerves, was to ascertain whether, when a current was impelled through a mass of muscle, any part of the current might have passed through the nervous filaments spread throughout that muscle. For this purpose I took a piece of muscle from the thigh of a rabbit, a dog, or a fowl which had been dead for sufficient time for muscular irritability to have ceased; I cut this mass of muscle with a knife, and introduced into the opening thus made the nerve of a highly sensitive galvanoscopic frog; I covered over the nerve and a part of the leg, endeavouring to envelope them perfectly in the piece of muscle. When the contractions, which often occur in the galvanoscopic frog itself immediately after it has been prepared, had ceased, I passed an electric current of from 25 to 30 elements of FARADAY through the mass of muscle, applying the poles to different parts of its surface. In whatever way I varied this experiment, provided I did not touch very close to the nerves of the galvanoscopic frog, this frog never entered into contraction, although a very powerful electrical current traverses in all directions the mass of muscle in which the nerve of the frog was contained. I have remarked already that in this experiment a mass of muscle must be employed in which all irritability is extinct, because if muscles are made use of which contract on the passage of the electric current, the galvanoscopic frog exhibits phenomena of *induced* contraction; we are convinced of this by observing that they cease when the muscular irritability has disappeared. We may therefore conclude from this experiment, that when the poles of a pile of 25 or 30 elements are applied to the surface of the muscles of a living animal, the phenomena produced by the passage of the current must depend either on the *direct* action of the current on the muscular fibre, or on the *indirect* action or *influence* of the electric current transmitted by the muscular fibre on its own nervous filaments, or, to express it more clearly, on the nervous force existing in these filaments.

Convinced of the great importance of this conclusion, I have varied these experiments in order to confirm them in different ways. I have already, in the commencement of this memoir, spoken of the difference of excitability produced in a nerve by an electric current according to its direction. This electro-physiological law is easily demonstrated by an experiment which I have detailed at some length in my memoirs*, and which is made by preparing the frog in the ordinary manner,—cutting it at the junction of the two thigh-bones, and then placing it astride between two glasses of water with one foot in one glass and one in another. When the two poles of the pile are plunged into the liquid (pure water) contained in the two glasses, it is obvious that one of the limbs is traversed by the electric current in the same direction as the ramification of the nerve, and the other in a contrary direction.

* Philosophical Transactions, 1846.

The experiment consists in this: that after fifteen or twenty minutes of the passage of the current, that limb only which is traversed by the inverse current, that is to say, in a direction contrary to the ramification of the nerve, contracts at the opening of the circuit.

When the frog is reduced to this state, if the nerve traversed by the inverse current is touched by a small portion of muscle, we see the limb instantly contract as if the circuit had been interrupted; and in fact the current ceases to pass through the nerve and enters the muscle on account of the greater conductibility of the latter substance.

I shall cite another experiment of the same kind. Having succeeded in modifying the excitability of the nerve by the passage of the current, as in the experiment just described, we can easily convince ourselves that this modification is confined to the exposed or isolated portion of the nerves. For if those portions of the nerves in both thighs, which had been previously buried in the muscles, be now laid bare, no alteration in their excitability is found to have occurred; but the altered excitability is limited to the pelvic portions of the nerves previously exposed and traversed by the current. It is evident that if the nerve, buried among the muscles of the thigh, were traversed by the current as its exposed portion above is, the modification of the excitability would extend through the whole length of the nerve. I repeat, therefore, once again, that when a muscular mass is traversed by an electric current, we are compelled to admit that no sensible quantity of that current is conducted by the nervous filament belonging to such muscle.

Another subject of research which has greatly interested me, and the exposition of which will precede that of the experiments which form the principal subject of this memoir, relates to the influence which the integrity of the nervous system exercises on the excitability of the nerves. In other words, supposing that a certain contraction is produced in the limb of a frog by the passage of a constant electric current through its lumbar nerves, would that contraction remain the same, or would it be increased or diminished were the spinal marrow to be cut? I had read in the 'Comptes Rendus' of the Academy of Paris an experiment by M. Bois Seguard, from which one would be led to conclude that the section of the spinal marrow increased the excitability of the lumbar nerve, at least during a certain period of time.

In order completely to satisfy myself on this point, which I consider as very important with regard to the theory of nervous functions, I was obliged to operate with the greatest possible exactitude, and to measure in every instance the contractions excited. In order to this I employed an apparatus invented by M. Breguet, the description of which I have given in my fourth memoir*. The results to be obtained from this apparatus are as exact as can be desired, provided the operation is carried on with sufficient patience, and that the necessary degree of practice has been acquired in the use of the machine. As it is necessary, in the first instance, that the current

* Philosophical Transactions, 1846.

should be constant, a WHEATSTONE's pile is the best adapted for the experiment. As the nervous filament by which the current is transmitted must be perfectly free from all trace of blood or other animal substance, it must be carefully cleaned, using a pair of forceps and lightly wiped with a piece of blotting-paper. It is also requisite that the gilded steel needle, which is introduced into the muscle of the thigh as nearly as possible to the insertion of the nerve, and which serves to complete the circuit, should, so far as is practicable, be always inserted in the same position in all the experiments. Lastly, care must be taken in choosing suitably the weight attached to the limb of the frog: if the weight be too small, the limb is not brought back to its position after contraction; on the other hand, if the weight be too great, the nerve is stretched, and the indications given by the apparatus are too small. I found that a weight of 0·600 gr. is the best adapted for the purpose.

I here give one of a series of experiments, undertaken with the view of resolving the question which I had proposed to myself.

I fasten a living frog to the clamp of the apparatus by passing a thread of silk round the thorax under the front claws: I then remove all the viscera of the abdomen, one of the limbs, and the muscles, as well as the bones of the pelvis: the frog, thus prepared, retains its natural liveliness for at least twenty or thirty minutes. I proceed to pass the *direct* current through the lumbar nerve, and I obtain contractions measured by the apparatus at 14°, 12°, 10°, 9°, 8°. I continue the passage of the current as short a time as possible, and close the circuits instantly after having opened them. The contractions first of all diminish rapidly, and then for a certain time they remain the same, if we are careful to leave the circuits closed as short a time as possible. When the deviation of the needle points constantly at 8°, I cut the spinal marrow of the frog, and pass the current again immediately: I have again the contraction 8° as before. I have frequently repeated this same experiment, and invariably with the same result. I also found that the duration of the contractions which persist the longest does not vary, in consequence of the section of the spinal marrow. It is therefore certain that the excitability of the nerve undergoes no immediate change after its separation from the nervous centre.

I then continued my investigations of this subject, conducting my experiments in a different manner from that already described, that is, by comparing the contraction of the muscular fibre excited by the passage of the electric current in a nerve which had been separated for several hours from the nervous centre, to that of another similar muscle the nerve of which had not undergone this operation.

It is hardly necessary to repeat, that, in order to the success of these experiments, BREGUET's apparatus must be used, employing the precautions already mentioned; the most indispensable of which is the careful removal of all traces of blood, &c. from the lumbar nerves of frogs submitted to these comparative experiments; they should also, as far as possible, be prepared in the same manner, so that their conditions should be similar.

I took the frogs as they came to hand, from among a considerable number, and divided the spinal marrow at about the middle. Twelve hours after this operation I began an experiment, preparing at the same time the frogs whose spinal marrow had been divided, and others which were intact.

In order that the comparison should be as perfect as possible, I employed successively in Breguet's apparatus for measuring contractions, two frogs, one of which had the spine divided, the other entire. In each experiment I operated on four frogs in the former, and four in the latter state. I made my experiments with a direct current, keeping the circuit closed as short a time as possible, and marking the variations of the needle of the dynamometer after ten or twelve passages of the current, because it is then only that the variations become constant; if the passage of the current in the same frog is prolonged, the variations gradually diminish; operating with a certain degree of dexterity, experiments on eight frogs may be completed in less than a quarter of an hour.

The following are the results of two experiments:—

Exp. 1.

Contraction of a frog the spinal marrow of which had been divided 12 hours.	Contraction of a frog with the spinal marrow entire.
16° to 14°	14°
18 20	18
18 16	12
20	12
20	12

Exp. 2.

After 18 hours.

24° to 22°	8°
22 24	10
22 16	12
17 16	12

According to these results, and others of the same kind, which it is unnecessary to give here, it is clearly proved by experiment that the contraction excited in the muscles of a frog, of which the spinal marrow has been divided from twelve to eighteen hours, is stronger than that which is obtained under the same circumstances from the muscle of a frog immediately after it is killed, without having been previously subjected to any alteration in its nervous system.

An observation which I had occasion to make in all my experiments, gave me some insight into the cause of this singular phenomenon. If a vigorous frog is rapidly prepared and subjected to experiment in the dynamometer, the first con-

tractions which are obtained are very feeble, particularly if the weight attached to the limb, to bring it back to its position after the contractions have ceased, be extremely small. If we continue to operate on this same frog, we see the contractions become stronger and increase during a certain time. In all cases the muscles of frogs killed and prepared rapidly, are stiff, and seized with a kind of tetanic contraction; while the muscles are in this state, the contractions which are obtained by the passage of the electric current are necessarily less strong than those which are developed when these same muscles have ceased to be contracted naturally.

After having repeated some experiments of this kind with the dynamometer, I soon came to the conviction that this was the real cause of the phenomenon under observation. I shall only give one of these experiments, which proves the truth of this explanation.

I operated on very vigorous frogs, four of which had had the spinal marrow divided twenty-four hours before experiment, and four other similar frogs which were intact.

The following are the numbers found immediately after the preparation :—

Contraction of the frog of which the spinal marrow had been divided for 24 hours.	Contraction of the frog in the natural state.
°	°
30	26
28	24
26	24
24	20

I left the frogs untouched for forty minutes, and then repeated the experiment: the following are the results :—

°	°
10	22
8	20
8	16
8	16

The difference of contraction obtained in the two experiments is therefore evidently due to the state of the muscles differing in the two cases, according to whether the frog was submitted to experiment immediately after death, or whether it had had the spinal marrow divided for a long time, and consequently the muscle relaxed for a considerable period. The contractions excited by the electric current in a frog immediately after death, are feeble at first, on account of the nearly tetanic condition of the muscles; whereas, if left in repose, so as to give time for the muscles to become relaxed, the contractions then excited by the current are stronger. The contrary to this occurs if the experiment be made on a frog the muscles of which have been for some time without contraction, in consequence of the spinal marrow having been

divided; the contractions are very strong at first, but they soon diminish in strength, and that rapidly.

It would therefore be a mistake to conclude that muscular contraction increases because the nerve traversed by the electric current has been separated from the nervous centre: we have seen what is the true explanation of the phenomenon, and that this conclusion is only apparent.

On the other hand, these experiments prove, as did also those of the preceding section, that the excitability of a nerve is not altered by its separation from the nervous centres, or, rather, that the only alteration which it undergoes consists in the increased rapidity with which the excitability diminishes under the action of stimulants. Thus, the contraction produced by the passage of an electric current through a nerve is sensibly the same, whether this nerve be in communication with the nervous centres, or separated from them for several hours, or an instant after the separation has been effected: when the action of the current is repeated, its effects diminish the more rapidly exactly in proportion to the length of time which has elapsed since the separation of the nerve from the nervous centre.

I think it is scarcely necessary for me to remark, that these conclusions are not contrary to those of Müller and Longet; according to which it was shown that when the nerves had been separated from the central mass, for weeks and months, the sensibility of these nerves and the irritability of the muscular fibre were diminished. M. Longet has given the interpretation of this phenomenon, grounded on experiment.

In order to complete the first part of this memoir, I now proceed to relate the experiments and considerations by which the strict analogy existing between electricity and nervous force, together with the nature of that analogy, are demonstrated in a most satisfactory manner.

At the beginning of this memoir, referring to my preceding researches in electro-physiology, I mentioned the law according to which, by the influence of the nervous current, a development of electricity takes place in the organ of electrical fishes. We shall now consider what may be called the converse of this phenomenon, that is to say, the development of nervous force under the influence of the electric current, which development is produced exactly according to the same law as that of electricity by nervous force. This influence of electricity on nervous force is manifested in the muscular fibre: we have already observed at the beginning of this memoir that the phenomena presented by the organ of electrical fishes, as well as those of the muscular fibre, together with the modifications of these phenomena under various circumstances, invariably followed the same course, and preserved the strictest analogy with each other, so that what was true with regard to the electrical discharge of the torpedo, was equally so with regard to muscular contraction.

This fact admitted, we proceed to the experiments.

Expose in a living dog, rabbit or frog, the muscles of the thighs, removing entirely the skin and membranes, then transmit through the muscles the electric current

from an ordinary pile of from 30 to 40 elements, applying one of the poles to the upper, and the other to the lower part of the thigh. If the positive pole is placed above and the negative below, the current traverses the muscle in the same direction as the ramification of the nerves; the contrary is the case if the position of the poles be reversed.

Experiments of this kind date from the earliest times of galvanism; but the difficulty in these researches of separating truth from error, that which is constant and invariable from that which is merely accidental, and, above all, the still imperfect state of electro-physiological science, have hitherto prevented the attainment of any positive conclusions.

In experiments on this subject, great precaution is necessary in order to be certain that the electric current does not traverse the nervous filaments of the muscle; this certainty is obtained, as we have already seen, by keeping the poles of the electrical pile in contact with the surface of the muscle, at the greatest possible distance from the nervous filaments which spread through its interior. We must carefully remove from the surface of the muscle all traces of blood or other liquids; and I have generally been in the habit of applying one pole to the upper and the other to the under surface of the muscle.

When the electric current traverses the muscular mass of the thigh of a living animal in the same direction as the ramification of the nerves, a very strong contraction always takes place, which contraction is excited not only in the muscle directly traversed by the current, but also in the inferior muscles of the leg and in the foot.

When the electric current traverses the muscular mass in the contrary direction to that of the ramification of the nerves, the animal utters loud cries, and gives other indications of suffering severe pain, accompanied by contractions much less violent than in the preceding case, and which never extend beyond the muscles traversed by the current.

If we were to satisfy ourselves with seeing these experiments once only, or were to confine ourselves to a few trials only, we might easily be led to form an erroneous conclusion; in fact, at the beginning of the experiment, particularly if a somewhat powerful current be employed, there are both cries of pain and contractions at the same time; but this soon ceases, particularly if we know how to regulate duly the strength of the current. The constant effects which distinguish the action of the electric current, according to its direction, in the muscles of living animals, are those which I have indicated, namely, pain, when the electric current is what is commonly called inverse,—contraction, when the current is direct.

Now, setting aside all hypothesis, there can be but one way of explaining these phenomena: when there is a contraction, there must necessarily be a current of nervous force propagated from the brain towards the extremities of the nerves: when there is a sensation of pain, this current must be impelled in a contrary direction, that is,

from the nervous extremities towards the brain. We must bear in mind that it has been demonstrated by direct experiments, that when an electric current is propagated in a muscle, this current never quits the muscular fibre in order to pass into the nervous filaments. It is therefore perfectly evident that the phenomena of which we have spoken, excited by the passage of the electrical current through a mass of living muscle, are exclusively owing to the *influence* of electrical states propagated in the muscles upon the nervous force contained in the nerves. To speak with more precision, we should say thus: it is demonstrated by experiment that an electric current transmitted through a living mass of muscle in the same direction as its nervous ramification, developes a nervous current which is propagated in the direction of the ramification of the nerve, and which reaches to its extremities; if the electric current pass in a contrary direction to that of the ramification of the nerve, the nervous current which it developes follows the same direction, that is, from the extremity of the nerve towards the brain.

The great importance of the conclusions drawn from these experiments consists in this, that they lead to the same law which establishes the analogy between nervous force and the electrical discharge of fishes.

We obtain an electrical discharge in fishes, when we produce a nervous current by stimulating the nerve which communicates with the organ. In experimenting on living animals, we produce a nervous current by the electric discharge which we transmit through the muscles. When this discharge is directed through the muscle in such a way as that the positive and negative states of electricity are disposed relatively to the ramification of the nerves, as in the discharge of electrical fishes, a nervous current is produced by the influence of the electric current having the same direction in both cases; in the torpedo, the nervous current produces the electrical states; in the muscular fibre, the nervous current is produced by the influence of the electric current.

Following up the analogy, we are led to expect that when the electric current traverses a muscular mass in a contrary direction to that of the ramification of the nerve, it would produce a nervous current in an opposite direction to that which is developed by the electric current passing along the muscle in the same direction as the ramification of the nerves. This is a conclusion the truth of which is clearly demonstrated by the phenomena of sensation or of pain, which are produced by the passage of the electric current in a contrary direction to that of the ramification of the nerves.

Satisfied to go forward with a slow but sure step in the vast and very obscure field of electro-physiological science, I cannot but regard as highly important the discovery set forth at the close of this memoir, of the strict correlation existing between the electric current and nervous force.

Pisa, June 1849.

Fig. 1.

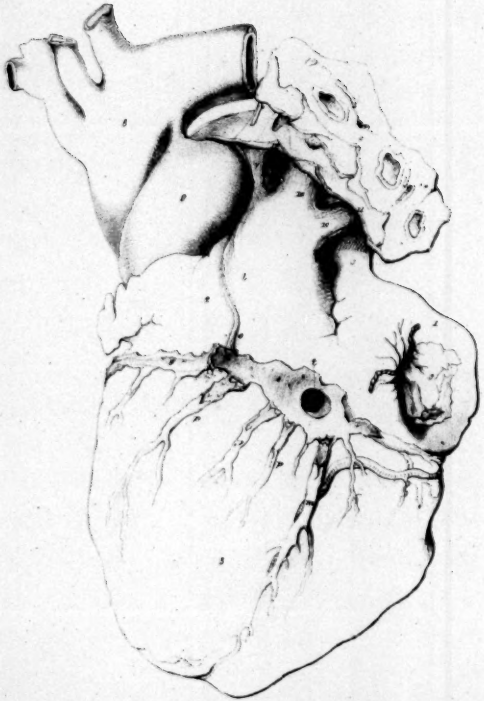

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Fig. 2.

natural size.

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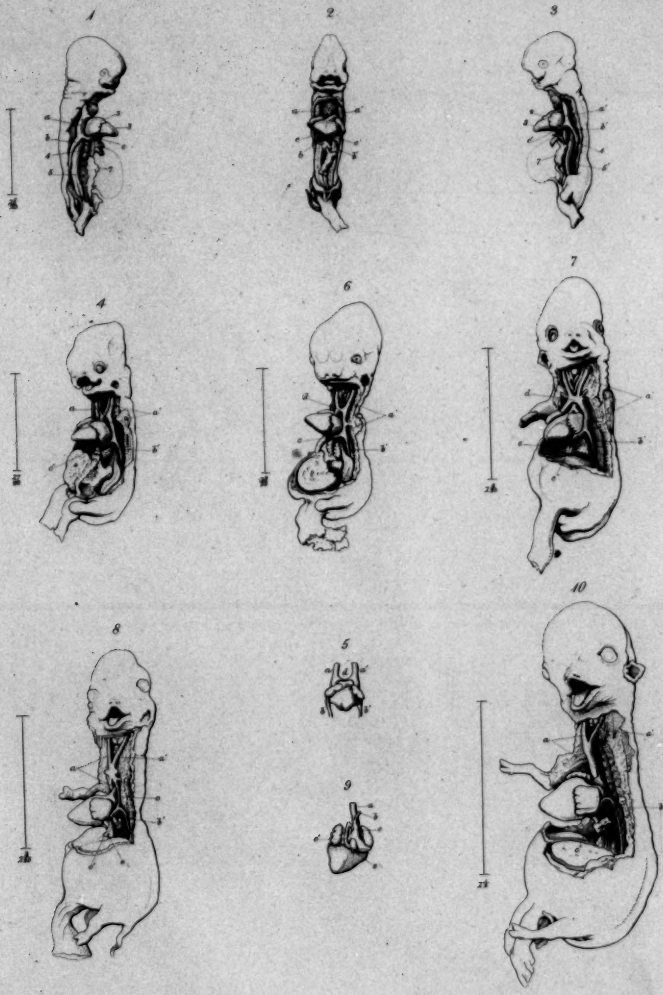

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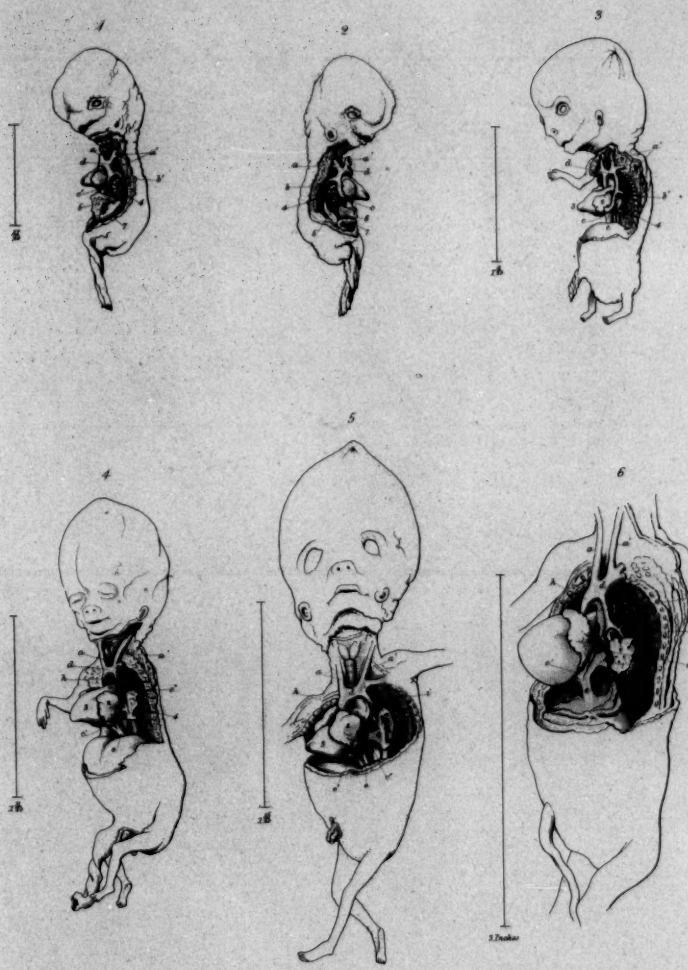
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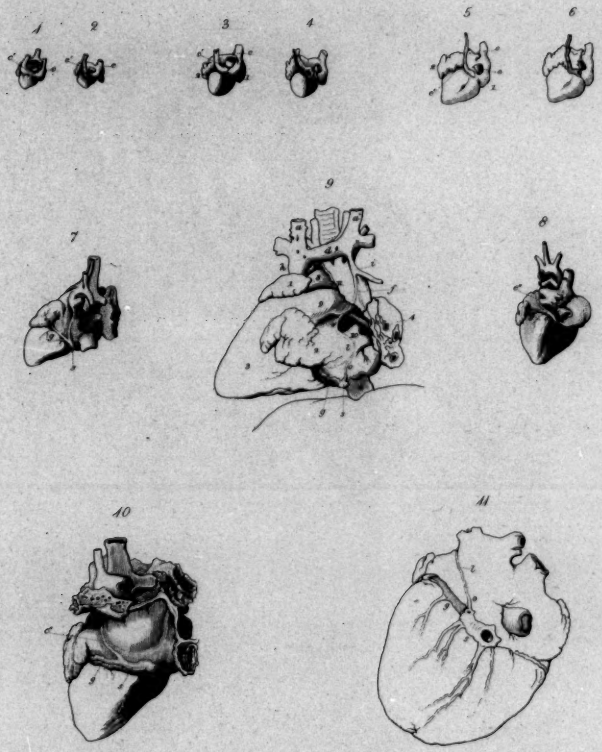

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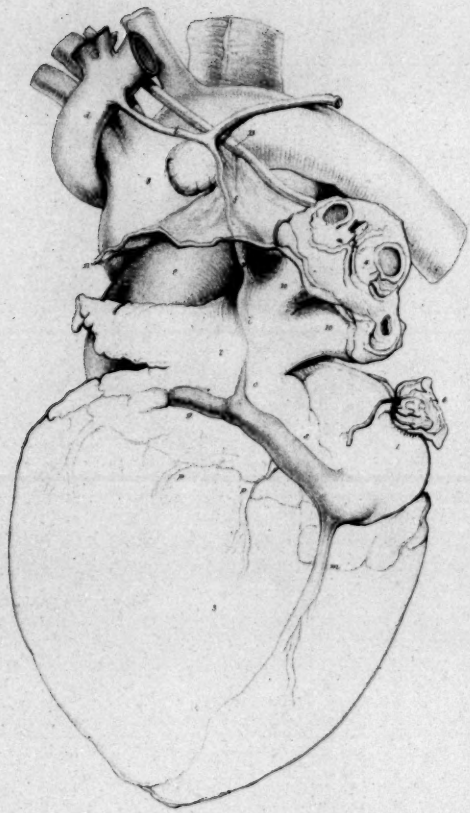

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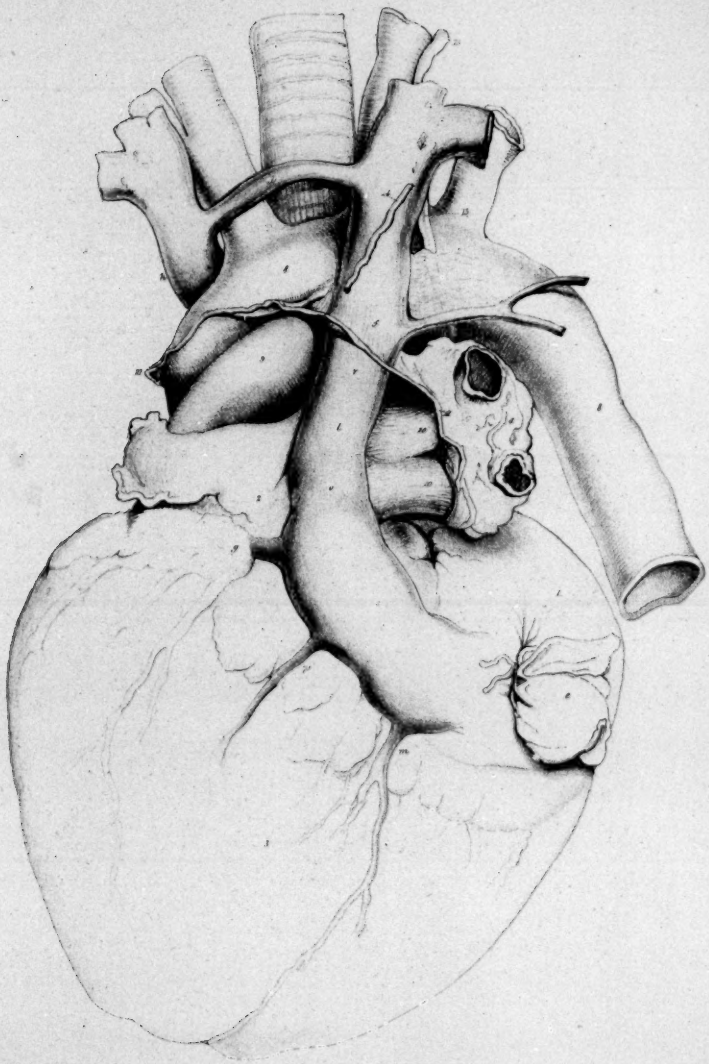

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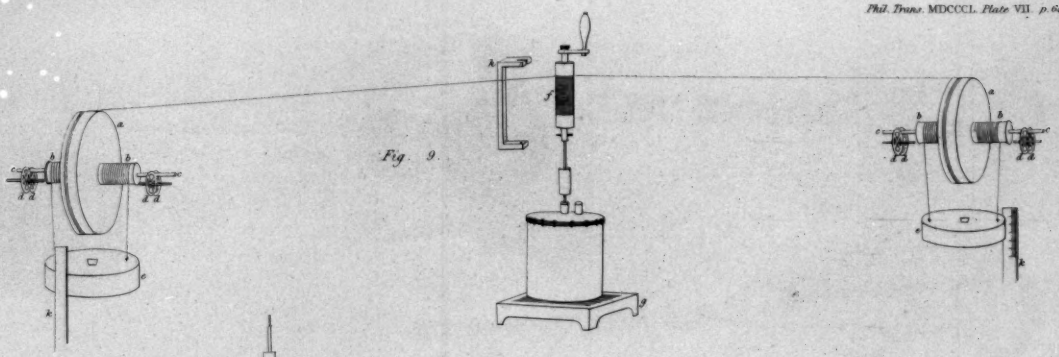

Fig. 9.

Fig. 1.

Fig. 2.

Fig. 3.

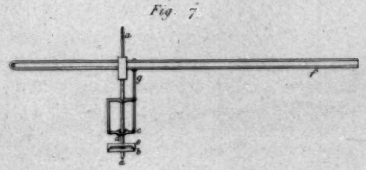

Fig. 7.

Fig. 5.

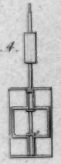

Fig. 4.

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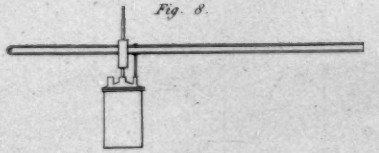


Fig. 8.

Scale One Inch to a Foot.

Mr. Joule on the Mechanical Equivalent of Heat.

J. Basire sc.

Fig. 1.

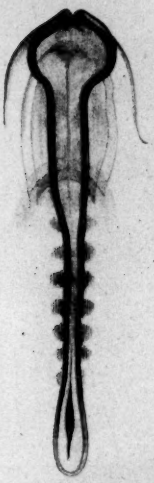
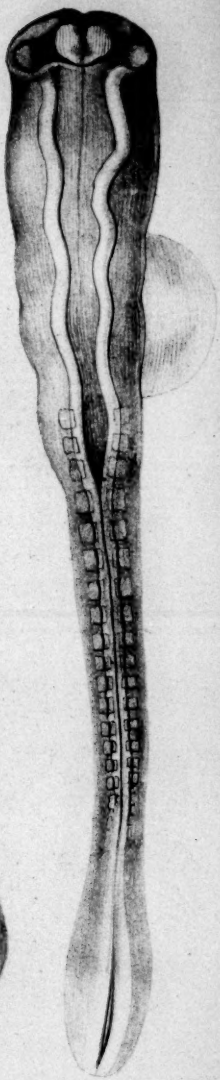
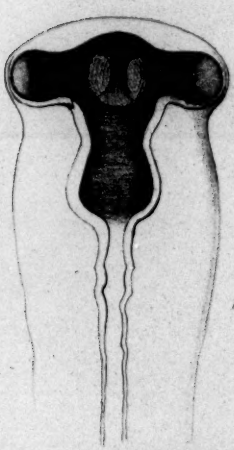


Fig. 2.

Fig. 3.

Fig. 4.





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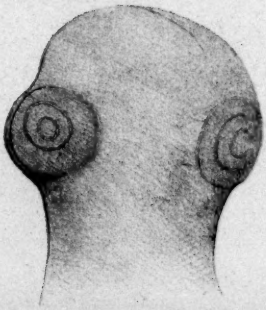

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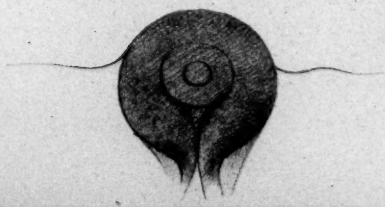

Fig. 7.

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Fig. 8.

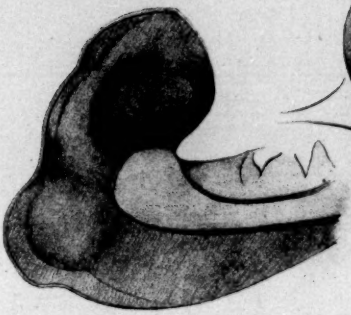
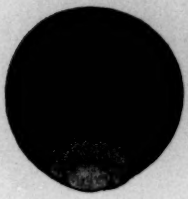


Fig. 9

Fig. 10.



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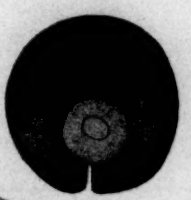

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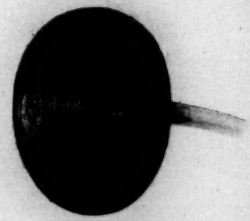
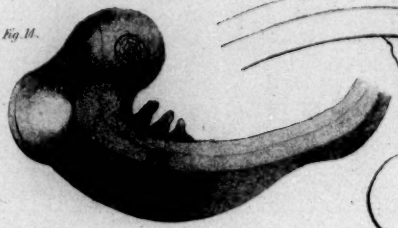


Fig. 13.

Fig. 14.



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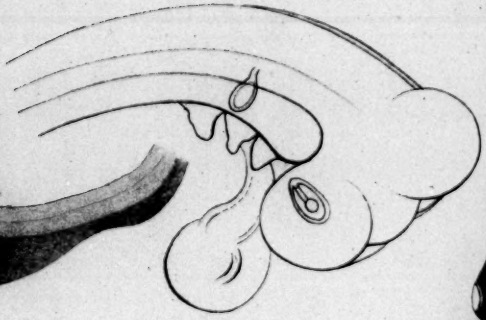

Fig. 17.

Fig. 16.

Fig. 18.

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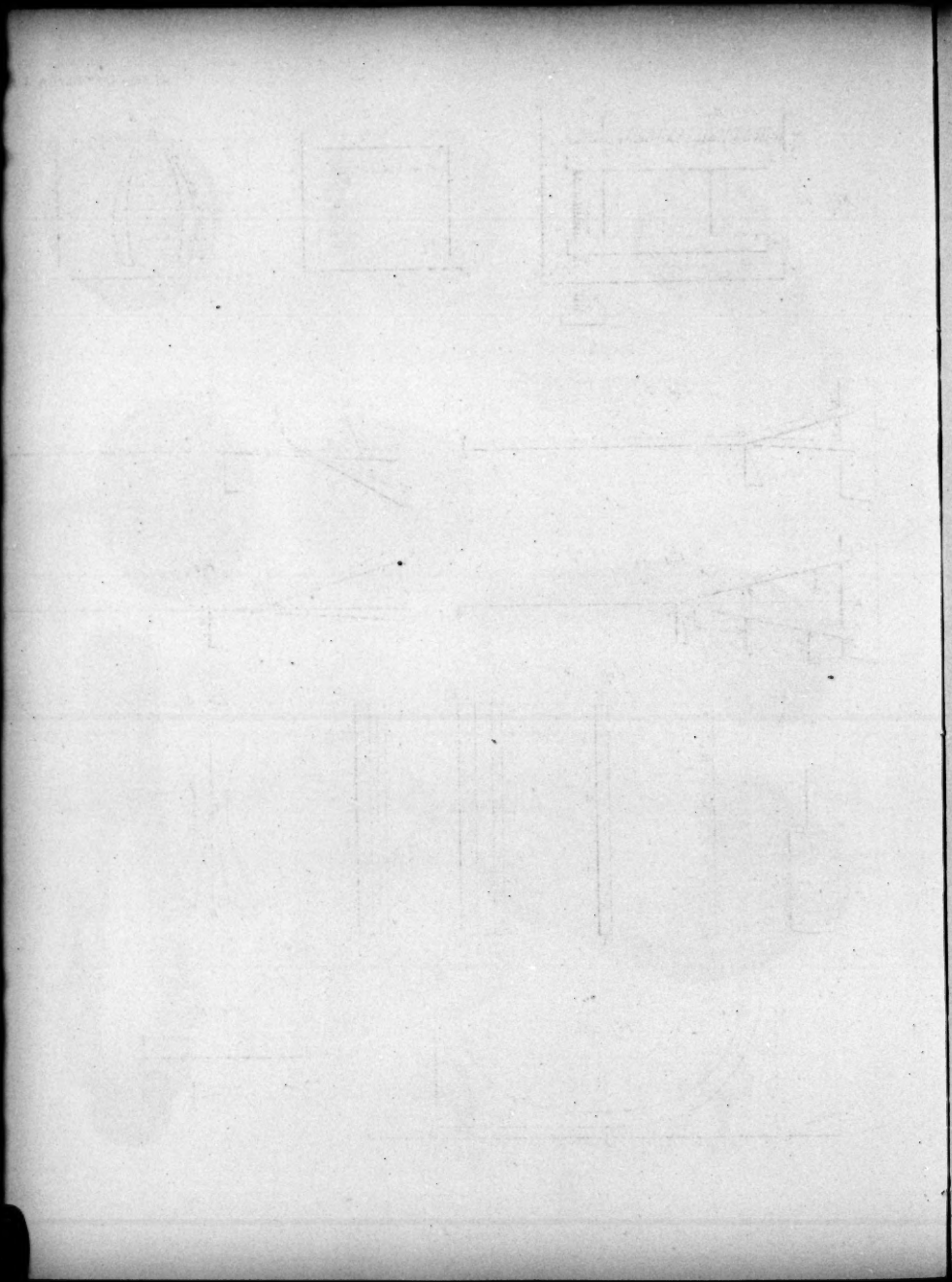

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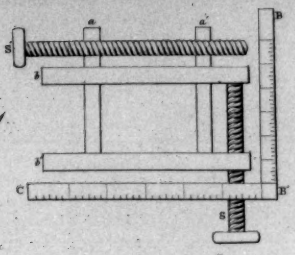

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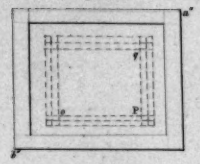

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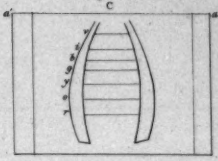

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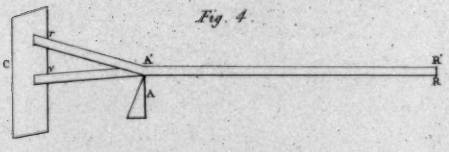

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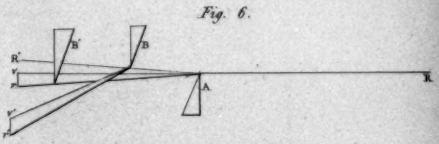

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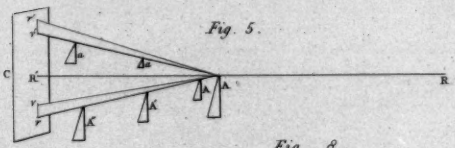

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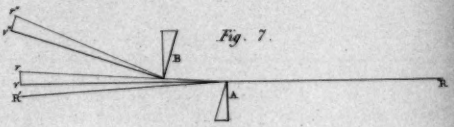

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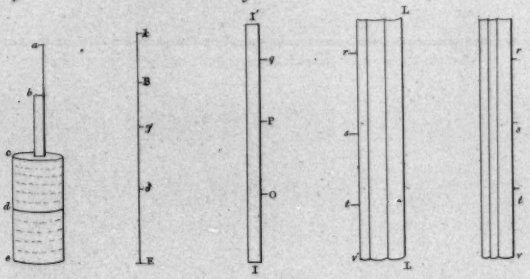

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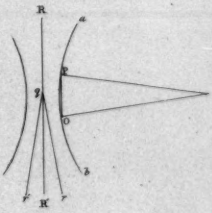

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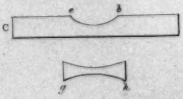

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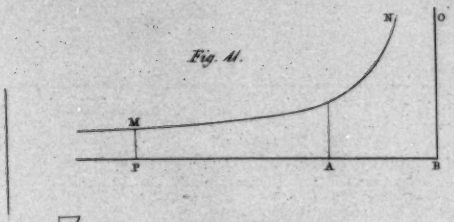

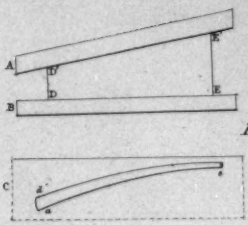

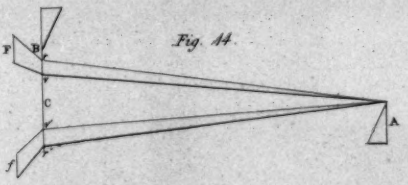

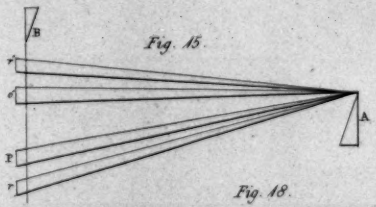

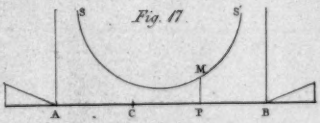

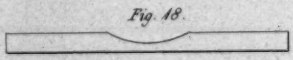

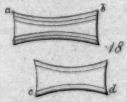

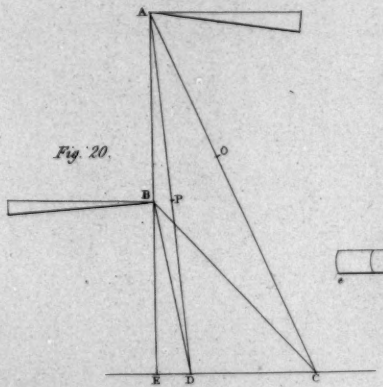

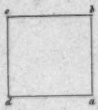

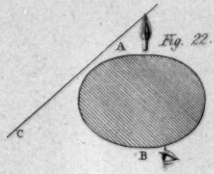

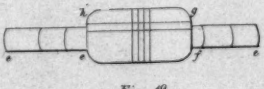

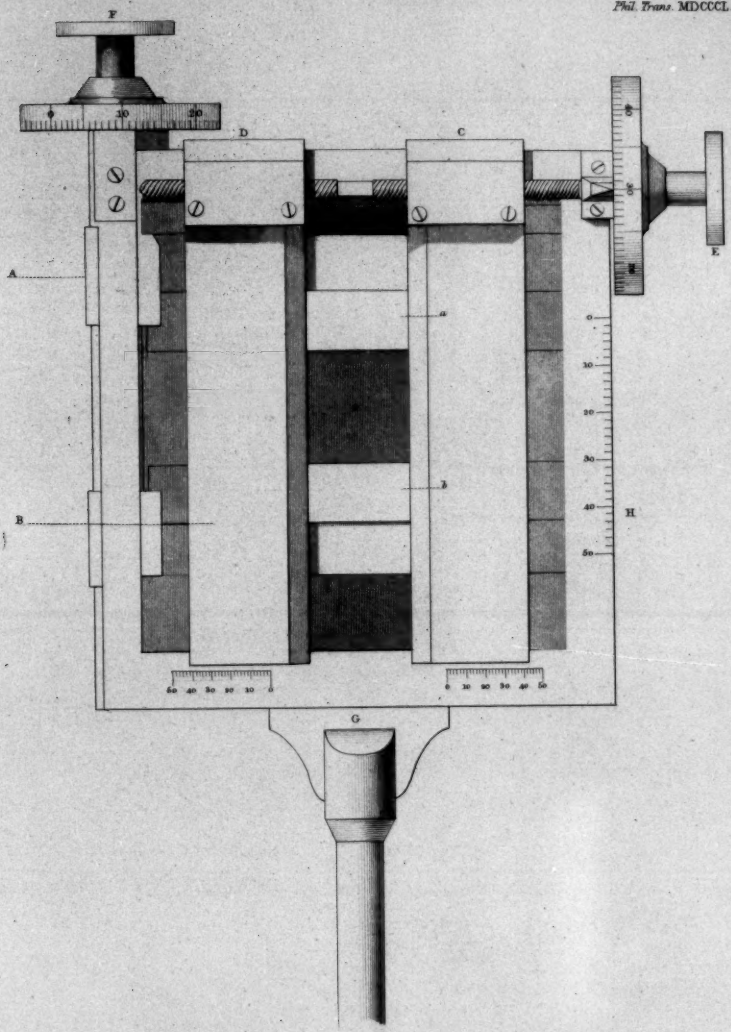

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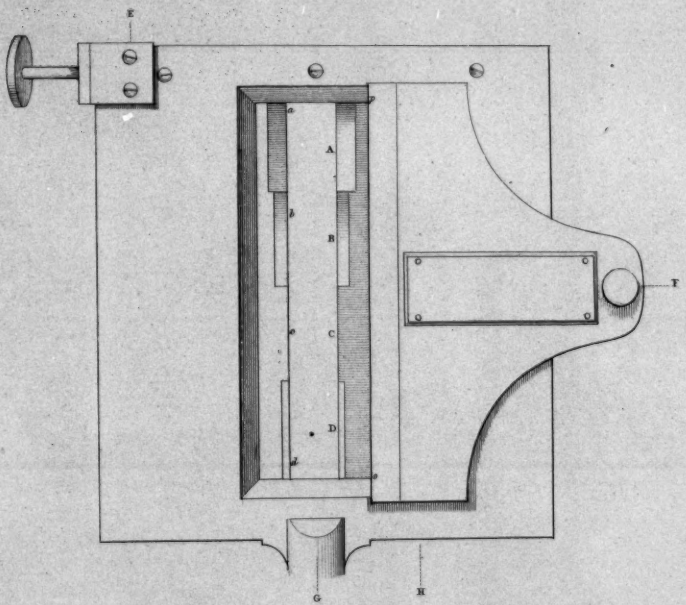

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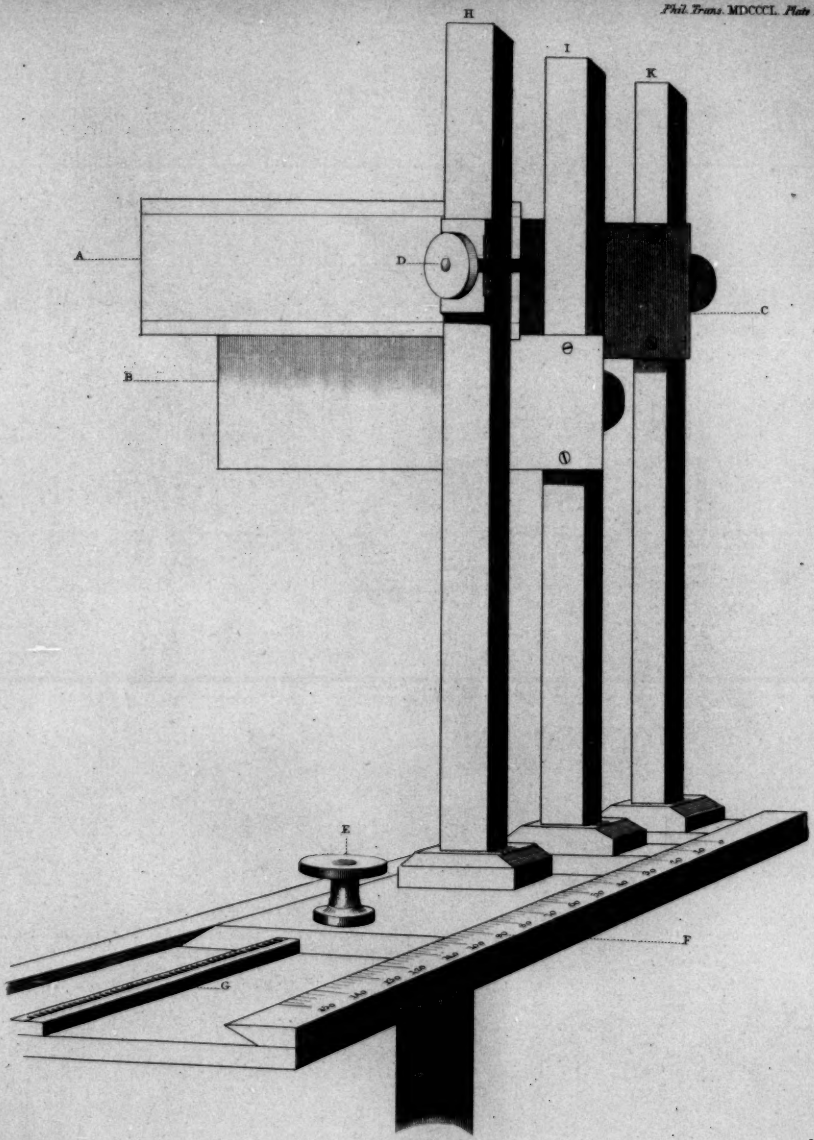

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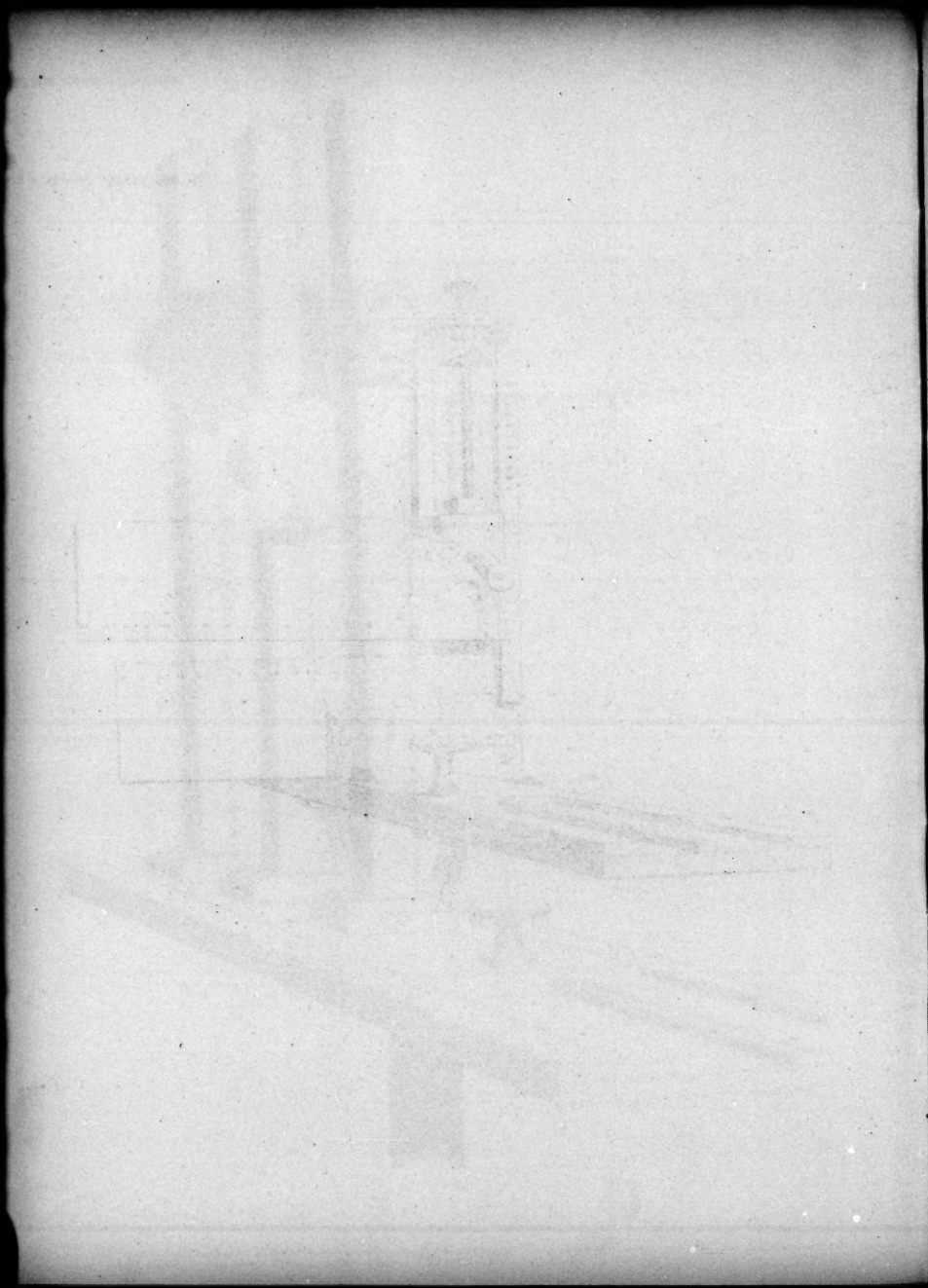

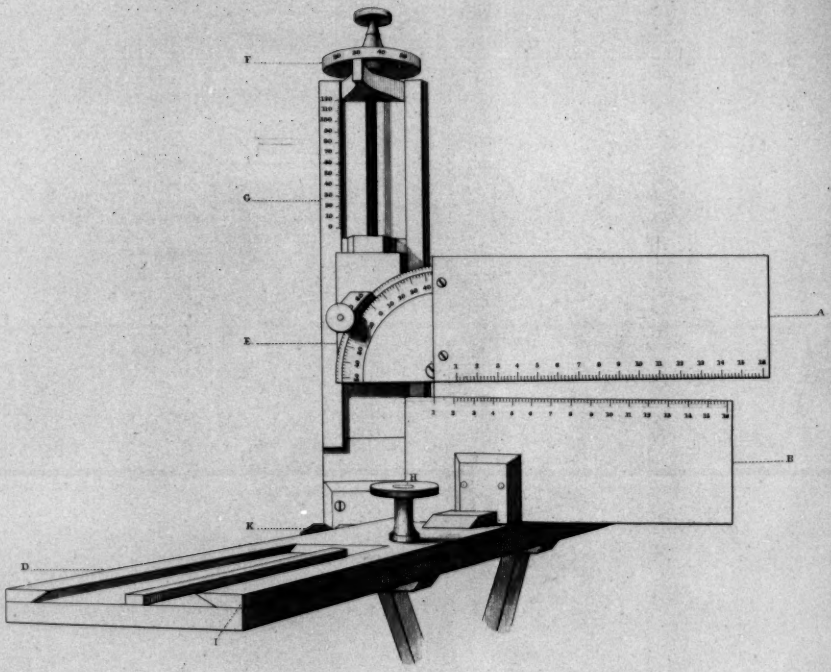

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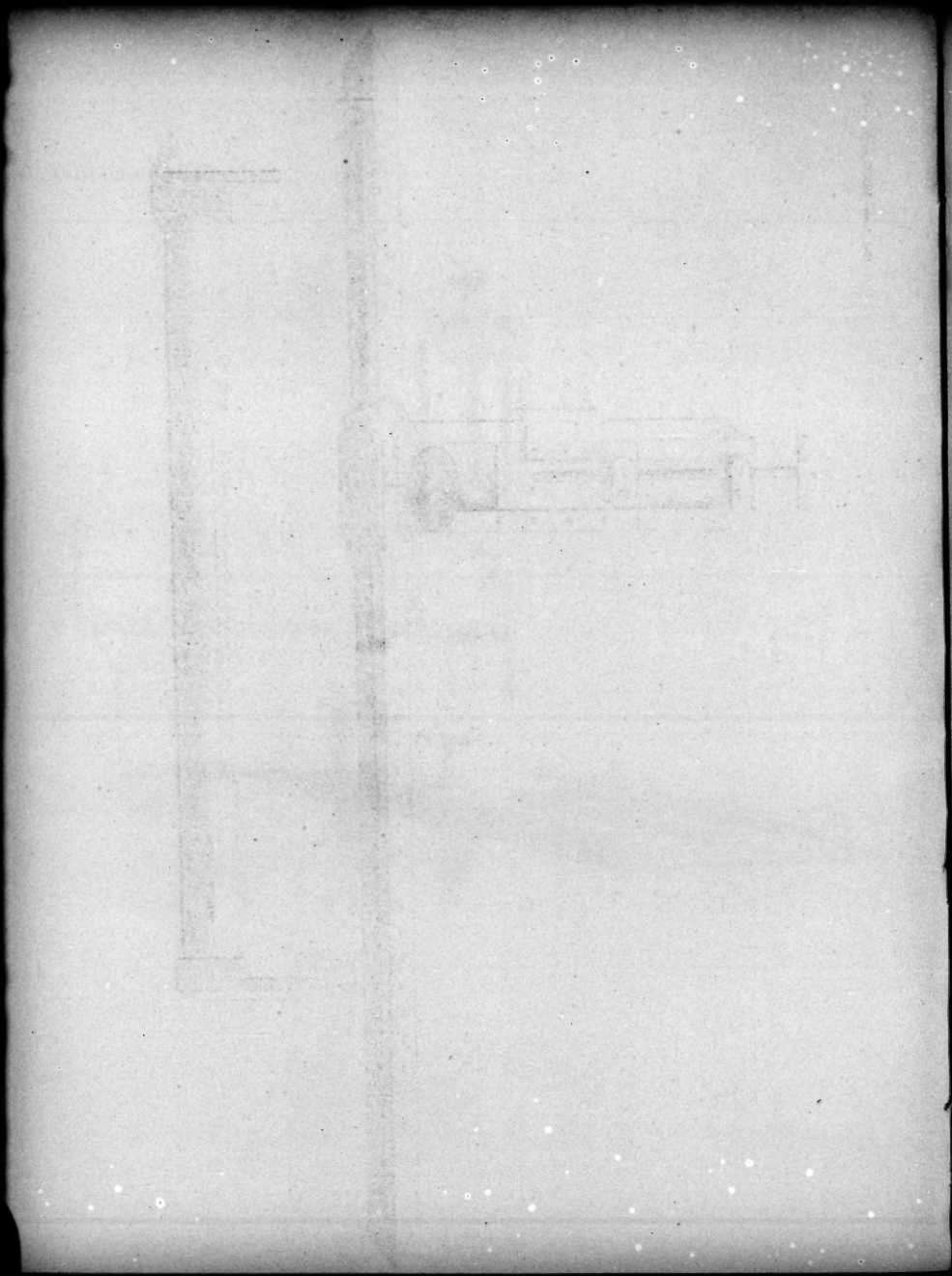

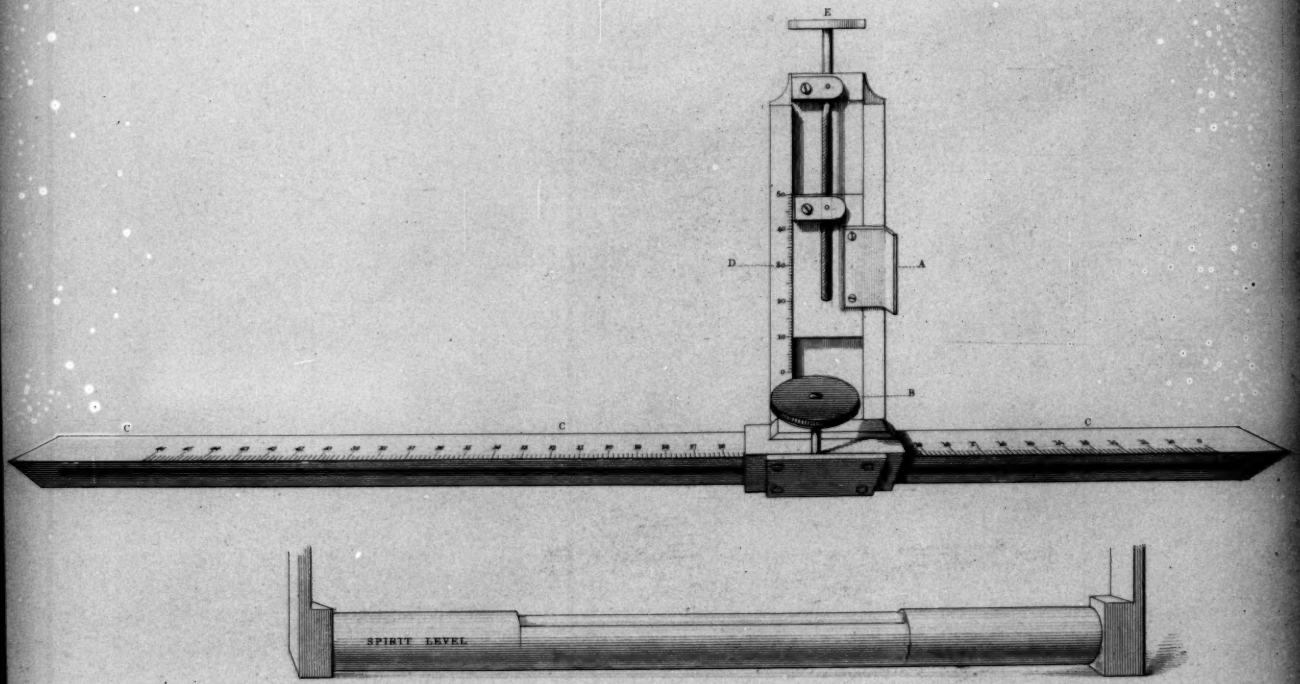

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